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Craig–Gordon model validation using stable isotope ratios in water vapor over the Southern Ocean

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S1 Sample collection and isotopic analysis

Atmospheric moisture was sampled using cryogenic cold trap, which is custom-made using pyrex tubes where atmospheric vapor was condensed with the help of a freezing mixture of liquid Nitrogen and Ethanol; maintained the temperature at $\sim$ -80°C. First, the inlet was connected to the Poly vinyl chloride (PVC) tube which was set at the forecastle of the ship at 15m above the water surface. The outlet of the glass trap was connected to a vacuum pump which is maintained at a flow rate of $\sim$ 250 ml/min. The line was flushed using the pump for at least $\sim$ 15 minutes before starting the collection process to avoid any sort of residual ambient air inside the tubing and the trap. An Ultra Torr connector (Swagelok) was connected from PVC tubing to the glass flask and from glass trap to the vacuum pump. The sampling time required for generating appreciable amount (2-3ml) of condensed water for isotopic analysis was $\sim$ 3 to 6 hours depending on the sampling location with greater sampling time at higher latitudes. After the sampling is done both ends of the glass flask was sealed using Parafilm to avoid any air inclusion inside the flask. Atmospheric moisture, condensed inside the cold trap as ice, was allowed to melt at room temperature ($\sim$ 15-20°C) and then transferred into 5 ml polyethylene storage vials. The samples were stored at 4°C. A similar setup for water vapor sampling was presented in earlier studies (Rahul et al., 2016, 2018).

Surface water samples were collected form Conductivity Temperature Depth (CTD) rosette when it was deployed and from a bucket thermometer used for measuring the sea surface temperature. Surface water samples were collected in 50ml High-Density Polyethylene air tight bottles.

All these samples were shipped to Bangalore for isotopic analysis and the measurements were carried out at the Centre for Earth Sciences, Indian Institute of Science, Bangalore. The protocol followed for the analysis of the gases after equilibration using a Finnigan Gas-bench II attached to a MAT 253 mass spectrometer is described in the (Rangarajan and Ghosh, 2011). For oxygen isotope analysis $200\mu L$ of water was transferred into an exetainer vial capped with butyl rubber septa and equilibrated with gas mixture 3% CO2+97% He for a period of 20 hours. For hydrogen isotopes, the water sample was equilibrated with gas mixture of 3% H2+97% He in presence of platinum catalyst (Hokko bead sticks) for a period of 80mins. The isotope ratios are expressed in ‰ using the standard δ notation relative to Vienna Standard Mean Ocean Water (VSMOW). Internal laboratory standards (OASIS-WWW, OASIS-LDK and OASIS-VOULEP) calibrated against the international water standards (VSMOW, Standard Light Antarctic Precipitation, and Greenland Ice Sheet Project) available from International Atomic Energy Agency in Vienna, were used to determine the accuracy and precision of the analysis. To account for intra batch calibration and drift correction, additional internal laboratory standards were measured in a batch. The overall analytical uncertainty on the measurements ($\pm 1\sigma$), as determined from replicate measurements of internal laboratory standards, were respectively ± 1.0‰ and ± 0.1‰ for $\delta^2 H$ and $\delta^{18} O$. Isotopic values are reported here with one standard deviation.

S2 Meteorological measurements

Atmosphere readings were taken via multiple instruments on-board the ocean research vessel SA Agulhas. Relative Humidity was calculated from the Psychrometric charts with the help of dry bulb and wet bulb temperature readings from sling Psychrometer with a range of -5°C to +50°C and a least count of 0.2°C. The expected accuracy in the relative humidity measurements from the psychrometer in 2-3%. Air temperature, Atmospheric Pressure, Wind's magnitude and Direction, GPS were logged from AWS (Automatic Weather Station) installed on board the ship. Salinity was measured using an Auto Salino Meter (Tsurumi Seiki Co. Ltd, Japan. Salinity values are expressed in the 1978 Practical Salinity Scale (PSU) (PSS-78) with a precision of ± 0.005 PSU. Sea Surface Temperature (SST) was measured using a bucket thermometer (Theodor Friedrichs and Co, Germany; accuracy $\pm$ 0.5°C).

S3 Supplementary figures and tables

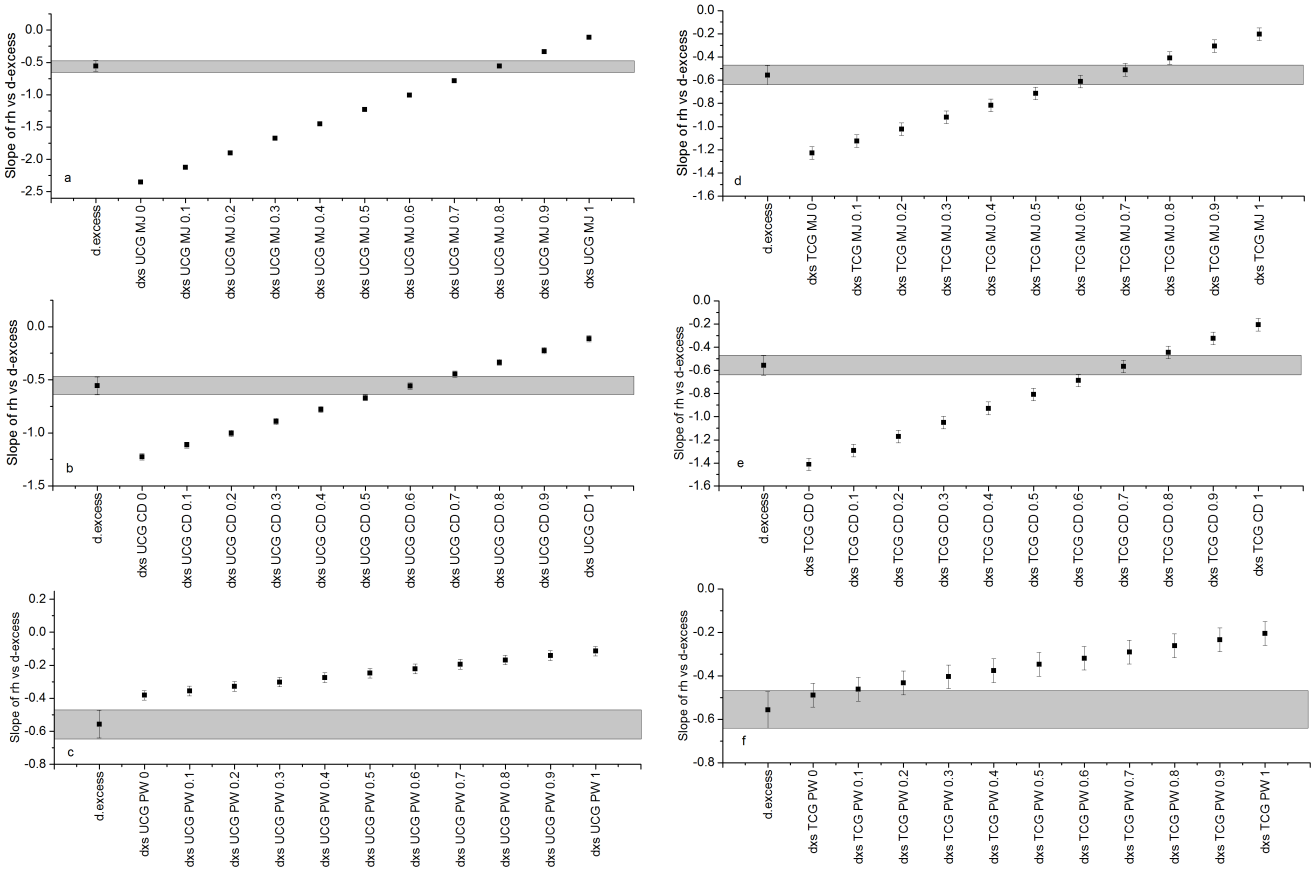

Figure S1. Slope of the relative humidity vs d-excess for the UCG (a-c) and the TCG (d-f) model runs (filled black squares) and the observed value (grey band).

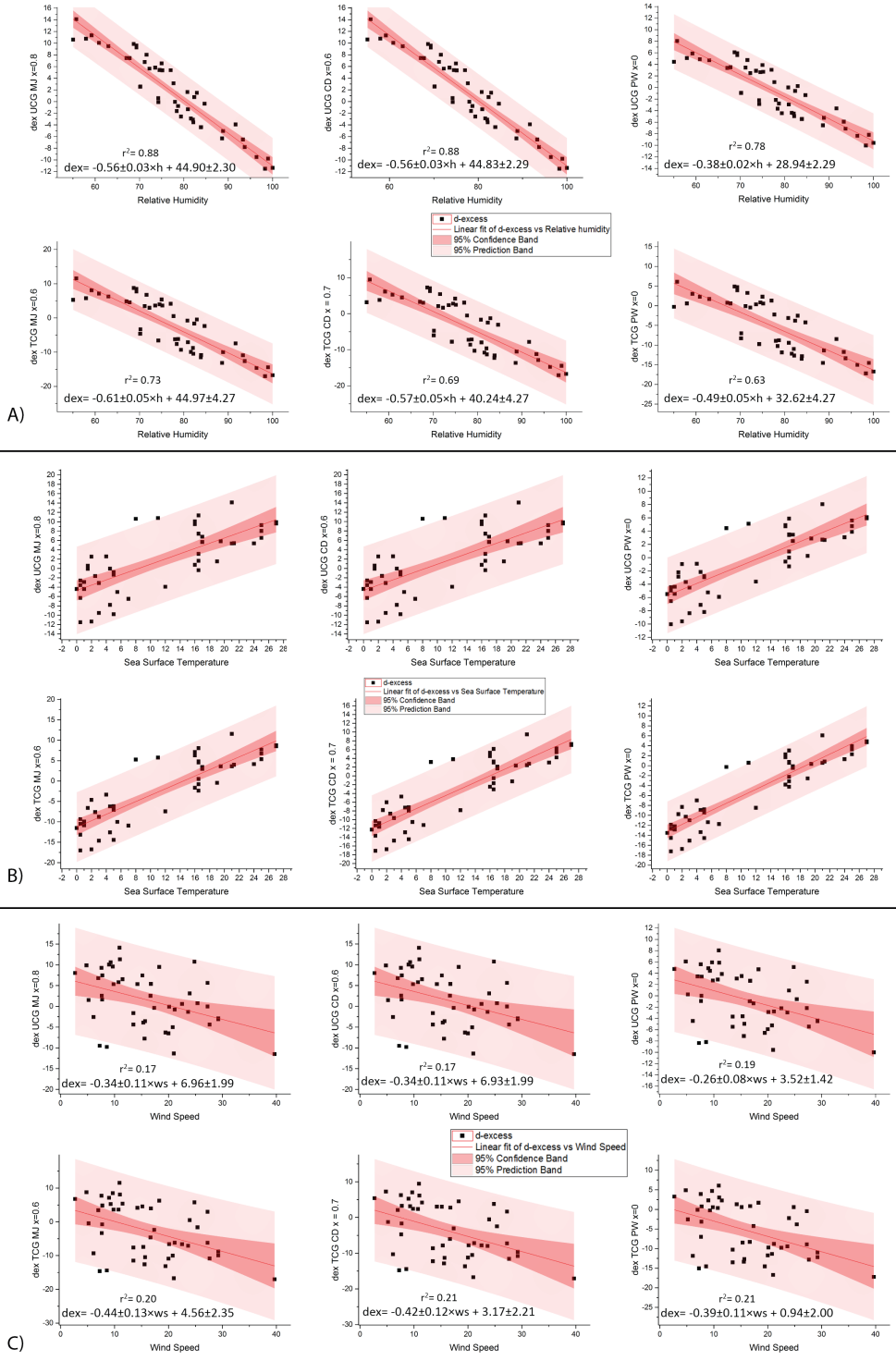

Figure S2. Linear regression equations between relative humidity (A), sea surface temperature (B) and wind speed (C) and the d-excess of the best-fit model runs. The dark and light pink shaded regions depict the 95% confidence bands and 95% prediction bands respectively.

Table S1. Slope, intercept and r^2 of the linear regression equations between meteorological parameters (relative humidity, sea surface temperature and winds speed) and $\delta^{18}O$ for different sample classifications. Also listed are the regression parameters for the data from Uemura et al. (2008)

Met. vs $\delta^{18}O$	Classification	Intercept		Slope		Statistics
		Value	Standard Error	Value	Standard Error	r^2
Relative Humidity	ALL	-11.43	3.43	-0.06	0.04	0.03
	ALL North of 65°S	-15.49	2.04	0.02	0.03	0.01
	ALL South of 65°S	-11.05	5.11	-0.12	0.06	0.15
	SOE IX North of 65°S	-12.37	2.59	-0.02	0.03	0.01
	SOE X North of 65°S	-18.95	3.39	0.06	0.04	0.07
	Uemura All	-20.61	2.81	0.05	0.04	0.02
Sea Surface Temperature	ALL	-18.43	0.53	0.27	0.05	0.33
	ALL North of 65°S	-15.47	0.40	0.12	0.03	0.27
	ALL South of 65°S	-19.38	0.71	-2.37	0.62	0.41
	SOE IX North of 65°S	-15.30	0.70	0.12	0.04	0.26
	SOE X North of 65°S	-15.52	0.51	0.11	0.05	0.19
	ALL SOE X	-16.82	0.42	0.19	0.05	0.33
	ALL SOE IX	-21.07	0.96	0.41	0.07	0.51
	Uemura All	-17.40	0.46	0.19	0.05	0.16
Wind Speed	ALL	-17.85	1.01	0.10	0.06	0.04
	ALL North of 65°S	-12.74	0.60	-0.09	0.03	0.13
	ALL South of 65°S	-23.76	1.40	0.25	0.11	0.21
	SOE IX North of 65°S	-12.62	0.77	-0.07	0.05	0.11
	SOE X North of 65°S	-13.05	0.98	-0.09	0.05	0.12
	ALL SOE X	-16.66	0.93	0.06	0.05	0.03
	ALL SOE IX	-18.77	1.80	0.14	0.12	0.04

Table S2. Slope, intercept and r^2 of the linear regression equations between meteorological parameters (relative humidity, sea surface temperature and winds speed) and $\delta^2 H$ for different sample classifications. Also listed are the regression parameters for the data from Uemura et al. (2008)

Met. vs $\delta^2 H$	Classification	Intercept		Slope		Statistics
		Value	Standard Error	Value	Standard Error	r^2
Relative Humidity	ALL	-57.14	27.50	-0.90	0.35	0.09
	ALL North of 65°S	-77.52	18.79	-0.42	0.24	0.06
	ALL South of 65°S	-41.57	22.20	-0.77	0.27	0.27
	SOE IX North of 65°S	-102.94	28.84	-0.18	0.38	0.01
	SOE X North of 65°S	-133.31	30.61	0.10	0.41	0.00
	Uemura All	-110.71	22.14	-0.16	0.28	0.00
Sea Surface Temperature	ALL	-149.02	3.84	2.76	0.34	0.49
	ALL North of 65°S	-128.58	2.78	1.68	0.20	0.61
	ALL South of 65°S	-127.93	5.09	1.76	0.31	0.60
	SOE IX North of 65°S	-128.31	3.31	1.41	0.30	0.50
	SOE X North of 65°S	-136.73	2.72	1.95	0.30	0.55
	ALL SOE X	-168.91	7.05	3.88	0.53	0.63
	ALL SOE IX	-154.43	5.43	-17.47	4.77	0.39
	Uemura All	-135.09	2.99	2.28	0.36	0.41
Wind Speed	ALL	-133.39	8.50	0.36	0.51	0.01
	ALL North of 65°S	-90.28	5.20	-1.24	0.29	0.29
	ALL South of 65°S	-85.84	6.89	-1.19	0.41	0.29
	SOE IX North of 65°S	-98.47	7.54	-1.04	0.40	0.23
	SOE X North of 65°S	-127.16	7.58	0.07	0.43	0.00
	ALL SOE X	-138.60	15.43	0.63	1.01	0.01
	ALL SOE IX	-182.36	11.09	1.49	0.85	0.13

S4 Data used in this study

Table S3. SOE-IX meteorological data, water vapor and surface water isotopic composition.

Date	**Lon**	**Lat**	**Tair** (^0C)	**Atm. Pres.** ($mbar$)	**Rel. Hum.** (%)	**Wind Speed** (m/s)	**SST** (^0C)	$\delta^{18}O$ (‰)	δ^2H (‰)	**d-excess** (‰)	**Sal.** (PSU)	$\delta^{18}O_{SW}$ (‰)
08/01/2017	57.50	-27.38	29.60	1015.80	69.31	9.68 –	27.0	-11.97	-83.04	12.71	35.59	
08/01/2018	57.52	-28.66	29.20	1014.80	68.69	4.80	27.0	-12.00	-80.79	15.17	35.50	
09/01/2017	57.49	-31.53	26.13	1016.50	69.31	7.58	25.0	-11.92	-82.11	13.22	35.54	0.31
09/01/2017	57.50	-32.26	24.13	1016.50	77.01	14.25	24.0	-12.16	-84.65	12.66	35.57	
09/01/2017	57.51	-33.44	19.83	1018.67	75.15	9.82	21.0	-12.22	-87.82	9.98	35.41	
10/01/2017	57.50	-35.38	21.50	1019.67	73.54	10.75	19.5	-12.29	-95.66	2.64	35.47	0.33
10/01/2017	57.51	-36.43	21.17	1017.67	82.94	5.20	19.0	-10.86	-82.74	4.16	35.46	
11/01/2017	57.87	-39.11	13.88	1018.25	72.25	27.25	17.0	-14.62	-104.60	12.36	35.58	
12/01/2017	58.41	-40.07	13.67	1027.83	60.86	9.00	16.0	-15.57	-107.66	16.89	35.41	
12/01/2017	57.94	-40.08	12.38	1028.00	67.06	7.75	16.5	-15.91	-109.99	17.33	35.51	
14/01/2017	58.52	-40.09	17.40	1017.80	82.36	25.40	16.0	-11.96	-91.18	4.52	35.36	0.38
13/01/2017	57.99	-40.21	13.00	1025.00	59.18	11.00	16.5	-14.88	-100.35	18.65	35.37	
15/01/2017	59.46	-41.38	14.17	1022.00	67.80	15.17	16.5	-14.37	-96.94	18.03	35.47	0.35
16/01/2017	61.15	-43.67	16.53	1023.83	71.16	7.00	17.0	-14.78	-101.41	16.85	35.49	-0.26*
16/01/2017	62.72	-45.46	11.67	1012.33	91.67	15.33	12.0	-12.37	-100.60	-1.60	35.52	
17/01/2017	64.00	-47.02	7.33	1003.33	93.33	20.00	7.0	-15.19	-129.06	-7.57	33.72	-0.12
18/01/2017	64.10	-49.02	5.60	1008.60	88.86	20.80	5.5	-13.97	-118.99	-7.20	33.52	-0.12
19/01/2017	64.17	-51.05	5.45	1011.67	78.70	21.17	5.0	-14.40	-117.37	-2.18	33.80	-0.07
19/01/2017	67.00	-51.73	4.79	1009.29	98.97	8.57	5.0	-12.97	-106.26	-2.52	33.69	
20/01/2017	68.49	-54.01	4.54	1006.57	93.73	15.57	4.5	-12.68	-101.07	0.37	33.87	0.05*
21/01/2017	69.29	-57.40	4.00	996.25	96.39	7.25	3.0	-13.39	-101.24	5.90	33.89	0.03*
22/01/2017	70.08	-61.95	0.98	970.20	100.00	21.00	2.0	-19.46	-162.93	-7.26	33.61	-0.07
23/01/2017	68.34	-64.00	0.14	976.17	98.31	39.67	0.5	-14.82	-126.91	-8.37	33.83	0.18*
24/01/2017	74.01	-65.99	0.09	983.00	95.57	14.86	0.5	-20.35	-160.07	2.72	33.86	
25/01/2017	72.54	-67.96	-0.51	992.14	96.45	20.57	1.5	-22.62	-182.23	-1.28	33.79	-0.61
26/01/2017	74.01	-67.99	1.00	991.33	72.19	7.67	1.5	-22.79	-177.95	4.41	33.43	
26/01/2017	74.00	-68.00	-0.33	992.00	83.67	12.00	1.5	-19.94	-154.85	4.66	33.21	
31/01/2017	76.00	-68.00	-1.75	978.00	94.23	5.83	1.5	-24.86	-193.54	5.31	32.73	
27/01/2017	74.05	-68.02	1.08	990.00	65.92	5.67	1.5	-23.33	-182.05	4.56	33.38	
30/01/2017	76.12	-68.04	-0.50	988.50	84.14	14.25	1.0	-22.17	-174.22	3.11	32.77	
27/01/2017	73.93	-68.21	0.12	988.40	80.13	8.20	2.0	-27.06	-221.38	-4.87	32.42	
28/01/2017	74.01	-68.60	-2.10	987.00	90.36	5.40	2.0	-27.47	-216.45	3.28		
31/01/2017	75.90	-69.19	-0.92	983.67	100.00	12.67	2.5	-24.25	-184.09	9.94	33.74	
01/02/2017	76.05	-69.34	0.33	991.33	97.92	7.33	0.0	-27.14	-211.65	5.46	32.07	
01/09/2018	74.73	-66.78	0.12	978.42	78.87	25.04	0.0	-17.54	-131.63	8.72	32.73	-0.57
01/02/2018	73.31	-66.80	0.74	989.95	76.64	8.75	0.0	-18.48	-142.40	5.41	33.37	-0.69

* The isotopic composition and salinity values of the surface ocean water are from different bucket samples.

Table S4. SOE-X meteorological data, water vapor and surface water isotopic composition.

Date	**Lon**	**Lat**	**Tair** (^0C)	**Atm. Pres.** ($mbar$)	**Rel. Hum.** (%)	**Wind Speed** (m/s)	**SST** (^0C)	$\delta^{18}O$ (‰)	δ^2H (‰)	**d-excess** (‰)	**Sal.** (PSU)	$\delta^{18}O_{SW}$ (‰)
12/10/2017	57.56	-21.98	26.13	1015.50	75.00	11.50		-12.34	-94.50	4.20		
12/11/2017	57.79	-26.80	28.55	1012.70	71.60	2.70	25.0	-11.46	-88.03	3.61	35.41	0.53
12/12/2017	58.00	-31.05	21.53	1016.00	74.53	16.76	21.5	-12.87	-101.43	1.52	35.42	0.77
13/12/17	58.20	-35.24	19.00	1015.00	55.75	10.93	21.0	-15.58	-110.07	14.54	35.56	0.36
14/12/17	58.49	-39.84	18.00	1007.13	80.82	7.72	16.5	-12.21	-98.43	-0.77	35.51	0.36
15/12/17	57.49	-39.99	14.46	995.03	84.68	17.36	16.5	-13.54	-100.92	7.39	33.84	0.61
16/12/17	58.80	-40.18	14.05	1015.04	63.00	18.29	16.0	-15.56	-110.40	14.11	35.47	0.28
17/12/17	58.38	-40.19	16.93	1016.80	77.68	23.94	16.5	-12.11	-97.43	-0.54	35.46	
18/12/17	60.50	-42.89	9.33	1011.52	57.95	24.82	11.0	-15.52	-115.67	8.51	33.95	
19/12/17	62.63	-45.69	8.07	1015.17	55.04	9.29	8.0	-16.56	-118.22	14.29	34.38	0.08
20/12/17	64.35	-48.07	6.94	991.67	80.92	23.65	5.0	-13.62	-112.24	-3.28	33.90	-0.41
21/12/17	63.85	-50.78	4.52	972.07	78.00	27.25	4.5	-14.31	-120.64	-6.12	33.81	-0.55
22/12/17	65.58	-53.07	4.79	970.60	70.21	7.64	4.0	-14.58	-121.16	-4.54		-0.02
23/12/17	68.23	-54.02	2.26	981.60	82.06	29.24	3.0	-15.81	-132.28	-5.76	33.90	0.02*
24/12/17	69.03	-56.43	2.80	993.74	78.40	13.49	2.5	-14.05	-118.57	-6.19	33.95	-0.01*
25/12/17	70.14	-58.03	3.18	1002.36	70.17	16.68	2.0	-14.44	-111.16	4.33	33.92	-0.57
25-26/12/17	70.12	-59.05	1.80	1002.17	82.14	15.67	0.5	-13.58	-108.05	0.60	33.08	-0.39
26/12/17	71.59	-59.99	1.21	993.15	83.82	13.50	0.0	-13.35	-112.80	-5.97	33.61	-0.48
26/12/17	71.14	-61.06	0.14	984.87	88.64	19.45	0.5	-13.93	-120.74	-9.32	33.68	-0.51
27/12/17	70.90	-61.66	1.19	985.72	79.35	6.12	0.5	-15.74	-129.25	-3.30	33.71	-0.20
17-18/01/18	57.49	-61.99	2.80	986.17	74.25	20.14	1.5	-15.39	-130.38	-7.28	33.70	
28/12/17	69.99	-63.01	-1.02	990.34	74.22	22.52	1.5	-21.18	-163.28	6.18	33.63	-0.59
17/01/18	57.52	-63.05	1.16	974.27	81.60	29.23	1.0	-16.63	-141.06	-8.01	33.49	
16-17/01/18	57.42	-64.01	1.90	969.20	83.90	27.63	1.0	-15.02	-130.43	-10.24	33.20	-0.22*
14/01/18	66.99	-65.49	-0.70	971.30	79.66	17.03	0.0	-15.40	-121.20	2.00		-0.35
16/01/18	57.85	-65.51	1.34	967.24	84.00	27.02	1.0	-15.70	-141.37	-15.73	33.57	-1.05*
30/12/17	74.91	-65.51	-0.36	978.48	76.16	6.21	0.0	-18.88	-148.91	2.15	33.39	-0.62
10/01/2018	68.81	-65.51	0.31	980.96	61.30	4.00	-0.5	-20.40	-151.04	12.15	33.69	-3.45*
31/12/17	73.84	-65.52	-0.40	984.47	74.00	14.10	0.0	-18.33	-152.82	-6.18	33.51	-1.16*
31/12/17-1/1/18	72.67	-65.54	-0.25	988.00	81.50	16.40	-1.0	-16.77	-157.86	-23.71	33.61	-0.80
15/01/18	57.26	-65.58	-0.33	973.95	72.66	11.08	0.5	-19.64	-155.75	1.40	33.48	
29-30/12/17	74.79	-66.35	-1.35	982.00	62.50	7.00	-0.5	-21.11	-161.02	7.88	32.99	-0.64
07/01/2018	74.98	-66.43	1.86	981.77	63.53	4.88	0.0	-18.17	-137.79	7.59	32.73	
01/01/2018	73.00	-66.45	0.90	987.10	77.67	5.60	-0.5	-17.65	-144.89	-3.72	32.73	-0.33*
09/01/2018	74.73	-66.78	0.12	978.42	78.87	25.04	0.0	-17.54	-131.63	8.72	32.73	-0.57
02/01/2018	73.31	-66.80	0.74	989.95	76.64	8.75	0.0	-18.48	-142.40	5.41	33.37	-0.69

* The isotopic composition and salinity values of the surface ocean water are from different bucket samples.

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