The CISE-LOCEAN seawater isotopic database (1998-2021)

Gilles Reverdin[1], Claire Waelbroeck[1], Catherine Pierre[1], Camille Akhoudas[1], Giovanni Aloisi[2], Marion Benetti[1], Bernard Bourlès[3], Magnus Danielsen[4], Jérôme Demange[1], Denis Diverrès[3], Jean-Claude Gascard[1], Marie-Noëlle Houssais[1], Hervé Le Goff[1], Pascale Lherminier[5], Claire Lo Monaco[1], Herlé Mercier[5], Nicolas Metzl[1], Simon Morisset[6], Aïcha Naamar[1], Thierry Reynaud[5], Jean-Baptiste Sallée[1], Virginie Thierry[5], Susan E. Hartman[7], Edward W. Mawji[7], Solveig Olafsdottir[4], Torsten Kanzow[8], Anton Velo[9], Antje Voelker[10,11], Igor Yashayaev[12], F. Alexander Haumann[13], Melanie J. Leng[14], Carol Arrowsmith[14], Michael Meredith[15]

1 Sorbonne University, LOCEAN - IPSL, CNRS–IRD–MNHN, Paris, France

2 Université de Paris, Institut de Physique du Globe de Paris, CNRS, 75005 Paris, France

3 UAR IMAGO, IRD, Plouzané, France

4 Marine and Fresh Water Institute, Iceland

5 University of Brest, LOPS, IUEM, UBO–CNRS–IRD–Ifremer, Plouzané, France

6 Amundsen Science, Québec, Canada

7 National Oceanogaphy Center, Southampton, UK

8 MARUM/Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany

9 Intituto de Investigaciones Marinas de Vigo, CSIC, Vigo, Spain

10 Instituto Português do Mar e da Atmosfera, Lisbon, Portugal

11 Centro de Ciencias do Mar, Faro, Portugal

12 Bedford Institute of Oceanogaphy, Dartmouth, Nova Scotia Canada

13 Atmospheric and Oceanic Sciences Program, Princeton University, Princeton, USA

14 British Geological Survey, Nottingham, UK

15 British Antarctic Survey, Cambridge, UK

Corresponding author: Gilles Reverdin, gilles.reverdin@locean.ipsl.fr

1 Abstract
2 The characteristics of the CISE-LOCEAN seawater isotope data set ($\delta^{18}O$, δ^2H, referred to as
3 δD) are presented. This data set covers the time period from 1998 to 2021 and currently includes
4 close to 8000 data entries, all with $\delta^{18}O$, three quarters of them also with δD, associated with a
5 date and space stamp and usually a salinity measurement. Until 2010, samples were analysed
6 by isotopic ratio mass spectrometry, and since then mostly by cavity ring-down spectroscopy
7 (CRDS). Instrumental uncertainty in this dataset is usually as low as 0.03‰ for $\delta^{18}O$ and 0.15‰
8 for δD. An additional uncertainty is related to the isotopic composition of the in-house standards
9 that are used to convert data into the Vienna Standard Mean Ocean Water (VSMOW) scale.
10 Different comparisons suggest that since 2010 the latter have remained within at most 0.03‰
11 for $\delta^{18}O$ and 0.20‰ for δD. Therefore, combining the two uncertainties suggests a
12 standard deviation of at most 0.05‰ for $\delta^{18}O$ and 0.25‰ for δD.
13 For some samples, we find that there has been evaporation during collection and storage,
14 requiring adjustment of the isotopic data produced by CRDS, based on d-excess ($\delta D - 8$ x
15 $\delta^{18}O$). This adjustment adds an uncertainty on the respective data of roughly 0.05‰ for $\delta^{18}O$
16 and 0.10‰ for δD. This issue of conservation of samples is certainly a strong source of quality
17 loss for parts of the database, and 'small' effects may have remained undetected.
18 The internal consistency of the database can be tested for subsets of the dataset, when time
19 series can be obtained (such as in the southern Indian Ocean or North Atlantic subpolar gyre).
20 These comparisons suggest that the overall uncertainty of the spatially (for a cruise) or
21 temporally (over a year) averaged data is less than 0.03‰ for $\delta^{18}O$ and 0.15‰ for δD. However,
22 18 comparisons with duplicate seawater data analysed in other laboratories or with other data
23 sets in the intermediate and deep ocean suggest a larger scatter. When averaging the 18
24 comparisons done for $\delta^{18}O$, we find a difference of 0.082‰ with a standard error of 0.016‰.
25 Such an average difference is expected due to the adjustments applied at LOCEAN to saline
26 water data produced either by CRDS or IRMS, but the scatter found suggests that care is needed
27 when merging datasets from different laboratories. Examples of time series in the surface North
28 Atlantic subpolar gyre illustrate the temporal changes in water isotope composition that can be
29 detected with a carefully validated dataset.
30

31
32   1. Introduction
33 Stable isotope analyses of ocean water (δ^{18}O, δ^2H later referred to as δD) were first discussed
34 by Craig and Gordon (1965) as tracers of water masses, and of the different components of the
35 global hydrological cycle, in particular the signals gained through evaporation, precipitation,
36 the interaction with sea ice, and continental water inputs, for example from the ice caps of
37 Greenland and Antarctica, and their ice shelves. Seawater stable isotopes have been used to
38 verify the circulation in ocean models and to characterize processes controlling their spatial
39 variability (Xu et al., 2012). Seawater isotopes have also been used to provide information on
40 the controls of the oxygen isotopic ratio of calcite plankton shells, in order to reconstruct past
41 ocean salinity and circulation. The GEOSECS program (Östlund et al., 1987) provided the first
42 consistent global dataset of seawater isotopes, but with a limited data coverage. The Global
43 Seawater Oxygen-18 Database at NASA GISS (Schmidt et al, 1999) has assembled most water
44 isotope data collected prior to 1998, with an effort to homogenize the dataset, when possible,
45 by estimating biases based on multiple measurements of deep-water samples (Schmidt, 1999;
46 Bigg and Rohling, 1999). A large part of the early analyses was done by isotope ratio mass
47 spectrometry (IRMS) and more recently using cavity ring-down spectrometry (CRDS). Walker
48 et al. (2016) illustrated that the two measurement techniques can provide equivalent results with
49 no obvious biases.
50
51 Since 1998, the isotopic platform facility at LOCEAN (later 'CISE-LOCEAN') has measured
52 seawater isotopic composition of samples collected on a series of oceanographic cruises or ships
53 of opportunity, mostly in the North Atlantic, the equatorial Atlantic, the southern Indian Ocean
54 and the Southern Ocean. This data set of δ^{18}O and δD of marine water covers the period 1998
55 to 2021, and is ongoing. Most data prior to 2010 (only δ^{18}O) were produced using an Isoprime
56 IRMS coupled with a Multiprep system (dual inlet method), whereas most data collected since
57 2010 (and a few earlier data) were obtained by CRDS, usually with a Picarro L2130-i, or less
58 commonly on a Picarro L2120-i. Occasionally, some samples were also run on an Isoprime
59 IRMS coupled to a GasBench (dual inlet method) at the university of Iceland (Reykjavik).
60 There are also a few pairs of samples measured on both systems. Most of these LOCEAN data
61 are not currently included in the Global Seawater Oxygen-18 Database at NASA GISS
62 (Schmidt et al., 1999), except for the 1998 OISO cruise data (note that earlier datasets measured
63 by co-author C. Pierre on other mass spectrometers preceding the current IRMS are included
64 in the NASA GISS database). Subsets of the LOCEAN data have been used in publications
65 (Akhoudas et al., 2020, 2021; Benetti et al., 2015; Benetti et al., 2017a; Benetti et al., 2017b;
66 Reverdin et al., 2019), where the subsets correspond to measurements at LOCEAN over a short
67 period with specific instrumental and analysis protocols. A regional surface North Atlantic
68 subset of the data was also presented in Reverdin et al. (2018b).
69
70 Here, we review the errors and uncertainties in this published dataset (Waterisotopes-CISE-
71 LOCEAN, 2021), and the extent to which the overall dataset of δ^{18}O, δD, and d-excess (d-excess
72 = δD - 8 x δ^{18}O) presented as ‰ versus V-SMOW, is internally consistent. We will also discuss
73 how the CISE-LOCEAN seawater isotopic database compares with other datasets, in particular
74 NASA GISS, and provide some overall statistics on the number of data and their distribution.
75
76
77   2. Uncertainties
78 We will first review the different sources of uncertainties relevant for this dataset, before
79 discussing the scale used and correction and flagging of data.
80

Uncertainties in the data reported originate from the water collection and storage in bottles (Sect. 2.1), the uncertainties resulting from the experimental laboratory set-up and analysis protocols (Sect. 2.2), and the uncertainties on the internal standards which are used in the experimental set-up (Sect. 2.3).

2.1 Collection and storage

At LOCEAN, we have mostly used glass-tinted bottles (volume 20 or 30 ml) with a hard cap including an internal rim to minimize water exchange through the cap (referred to later on as 'common' cap). No independent internal stopper or insert is used, and the bottles are not collected full. For some, but not all, cruises, the cap has been secured with parafilm after sample collection. When arriving in the laboratory, samples are commonly stored in a cold room or in a refrigerator at 4°C, except when the analysis is expected within 3 months after the arrival of the samples. The analysis has commonly been done within 1 year to 18 months after collection, and for some subsets such as for SURATLANT (Reverdin et al., 2018b), the analysis was usually done within 3 months after collection. However, due to various changes at LOCEAN, there has been at times a long backlog, with some samples having been stored in the cold room for 5 years or more. The longest storage time was for OISO-18 data collected in 2010 and analyzed 9 years later in 2019. Storage time was also very long for most samples of cruises OISO-21, OISO-22, OISO-23, OISO-25 and OISO-26 (South Indian Ocean, 2012 to 2016). Before analysis, samples are checked for obvious signs of evaporation, such as low water level or salt crystals around the bottle's neck.

We tested whether the samples in 'common' cap bottles change during storage by aging three reference waters of the same deep equatorial Atlantic origin over two years in a laboratory room which is not air-conditioned and without securing the 'common' caps with parafilm. Water is extracted every three months for isotopic analysis, which so far over 23 months has not revealed any significant drift, certainly not larger than 0.02‰ in $\delta^{18}O$ and 0.1‰ in δD. We expect that drifts would be even smaller when samples are stored at 4°C or with parafilm, if the caps are properly tightened.

In 2019, new caps were introduced which were not rigid and would often not provide a tight seal, with very large sample evolution over less than a year, sometimes reaching close to 1‰ in $\delta^{18}O$. This was the case in particular for the samples collected on M/V Nuka Arctica in April 2019 resulting in 32% of samples with suspected water vapor exchange (indicated by unexpected low d-excess and high $\delta^{18}O$; we verified this hypothesis by aging water in bottles with this cap, which also showed large drifts after three months at room temperature).

Even for bottles with the 'common' caps, issues of poor conservation have been suspected in some cases, in particular after long storage (typically, for 5 years or more). There is also the possibility that water vapor exchange has happened during transport, in particular when the samples have experienced very high temperatures, for instance for cruises ending in tropical ports and with long storage times in containers. This issue was probably the case for samples from the EUREC4A-OA cruise collected in February 2020 (Stevens et al, 2021) with an almost two-months storage in a container placed without sun-shielding in Pointe-à-Pitre (Guadeloupe, France), for which close to 22% of the bottles with no parafilm securing the cap are suspected to have signs of evaporation (during analysis, we noticed that the cap was often not tightly closed; their isotopic values also contrasted with the ones from special tightly closed nutrient vials pasteurized at 80°C for 40 minutes after collection that did not present any anomalous d-excess). There are also other subsets with data presenting obvious evaporation issues. The extreme case is for samples collected on M/V Nuka Arctica in 2018 and 2019, for which we

suspect evaporation for 20% of the water samples. In this case, the water was transferred from salinity bottles during the salinity analysis to be stored in bottles with the 'common' cap, where they stayed for close to 18 months before analysis.

2.2 Laboratory measurements

2.2.1 Method and protocol of analysis

Until 2010 and exceptionally later, the seawater samples $\delta^{18}O$ were directly measured on an Isoprime IRMS coupled to a Multiprep system (dual inlet method). A typical run lasted more than 24 hours, with a few in-house standards interspersed in the run. Drifts in the values corresponding to the internal standard used at the time ('Eau de Paris', referred to as EDP) were corrected for, assuming that the correction is not dependent on salinity or isotopic value. When checking the records, we found that $\delta^{18}O$ drift between successive EDP samples were often larger than 0.05 ‰. Uncertainty on correcting these drifts probably is on the order of 0.05‰.

Since late 2011, CRDS has been used, which simultaneously measures the samples $\delta^{18}O$ and δD. Each sample is vaporized, then injected in the cavity, a process repeated 6 to 12 times. The average and standard deviation (SD) of the sample's $\delta^{18}O$ and δD are computed out of the last (2 to 8) injections after stabilization is reached (Skzypek and Ford, 2014). This technique is applied to minimize the contamination from the previous sample, even though such memory effects should be small, in particular for $\delta^{18}O$ (Lis et al., 2008; Skrzypek and Ford, 2014; Vallet-Coulomb et al., 2021). The SD computed on the 2 to 8 selected injections is taken as an estimate of the instrumental error on the sample's $\delta^{18}O$ and δD measurements.

When a Picarro CRDS was first used at LOCEAN between 2011 and 2015, samples were distilled, and the measurement was thus done on freshwater (see Benetti et al., 2017c, for the average effect of the distillation on isotopic composition). Since 2016, seawater samples have been most often directly measured using a wire mesh (liner) to limit the spreading of sea salt in the vaporizer (https://www.picarro.com/sites/default/files/Salt%20Liner%20App%20Note_180323_final.pdf).

We most commonly used a Picarro L2130-i CRDS, but at times, a Picarro L2120-i CRDS was used, resulting in a larger standard deviation, in particular for δD. On both CRDS analyzers, when repeatability of the different injections of the sample was not sufficient or the daily run presented an unacceptably drift, the samples were analyzed at least a second time. In that case, either the best value or an average of the different values was retained.

The typical daily run at LOCEAN currently includes one or two reference water samples followed by three freshwater standards at the beginning to establish a slope calibration, as well as regularly interspersed reference water samples afterwards (usually, from KonaDeep mineral water with a value close to 0.8‰ in $\delta^{18}O$ and 2.0‰ δD). In addition to these freshwater in-house reference materials, a series can contain up to 12 isotopically-uncharacterized water samples, using a little over 1 ml of the sample placed in a cap-closed vial. Until 2015, when samples were distilled, series typically included 12 water samples. Since 2015, when salt water was directly placed in the vials, we have mostly run not more than 9 samples in a run, because the deposit of salt in the liner induces water retention or release, and thus noise in the measurements after roughly 60 injections of salty samples, as well as drifts in the reference water (Fig. 1a, b) and possibly slope calibration. Another source of drift is the appearance of

180   condensation on the top cap of the vials after a few hours, which will result in enriching the
181   residual vial water, although it is very likely a small source of drift.
182
183   Each seawater sample is injected 6 times, and the internal standards are injected usually 9 to 12
184   times at the beginning and end of the run. Whenever possible, samples expected to be in the
185   same range of values are placed together in the run to minimize the memory effect on the CRDS
186   which is largest for δD. We reject the first injection, as well as later injections if they are not
187   stable, retaining between two and eight injections that we average. Two methods were tested,
188   an empirical one, when we look for successive injections of the sample with close values
189   (typically 0.02‰ in $\delta^{18}O$), and the systematic selection of the values within 1 SD starting with
190   the last three injections. The retained injection values are then averaged. Differences in the
191   estimates produced by the two methods is usually within 0.02‰ in $\delta^{18}O$ (0.10‰ in δD for the
192   L2103-i). In the current database, the data retained are the ones obtained with the empirical
193   approach.
194
195   If a significant drift in the reference water values is noticed throughout the run, it is corrected,
196   usually by adjusting the data linearly between the successive values of the reference water (Fig.
197   1c, d). We thus assume that the estimated drift is independent of the $\delta^{18}O$ and δD values. In
198   addition, between 2017 and 2019, the response slope of the Picarro CRDS was adjusted by
199   interpolating between the three-point slope estimate (based on 3 internal standards) at the
200   beginning and at the end of the runs, when that was deemed possible. However, this adjustment
201   was discontinued in 2020 because the last internal standard samples were often not as reliably
202   measured, with values more sensitive to the number of injections, probably as a result of salt
203   deposits in the liner. Since 2020, we only check the instrument's response at the end of the run
204   with one of the freshwater internal standards.
205
206   Accuracy is best when samples are distilled, and for δD it is better on the Picarro CRDS L2130-
207   i compared to the Picarro CRDS L2120-i. Usually, the reproducibility of the $\delta^{18}O$
208   measurements between the different selected injections is within ±0.05‰ and reproducibility
209   of the δD measurements is within ±0.15‰, which should be considered an upper estimate of
210   the random error on a measurement with the Picarro L2130-i CRDS. Samples with a SD larger
211   than 0.06‰ in $\delta^{18}O$ were considered too uncertain and were rerun, as well as often (after 2015)
212   the first and last samples of each run.
213
214   In addition to the instrumental error of each sample's $\delta^{18}O$ and δD value described above, other
215   uncertainties arise from the data processing and conversion of measured $\delta^{18}O$ and δD to the
216   Vienna Standard Mean Ocean Water (VSMOW) scale. These additional sources of
217   uncertainties are detailed in the next sections.
218
219
220   2.2.2 Data processing
221   For the Picarro CRDS, a second source of uncertainty () is due to the way we process the data
222   of a daily run with salty water samples. As mentioned above, we first adjust the values to
223   compensate for the drift in reference water. Usually, this drift during the run is relatively small,
224   not exceeding 0.10‰ in $\delta^{18}O$ and 0.6‰ in δD, but in about 10% of the runs, it exceeded 0.20‰
225   in $\delta^{18}O$ over the whole run, or 0.10‰ in $\delta^{18}O$ over successive reference water samples (23 out
226   of 214 daily runs over which statistics were established from 06/2020 to 04/2021). When these
227   large changes are encountered, the run is estimated noisy and is usually rerun. However, even
228   for the other runs, a drift is usually observed with salty samples, and it often is a positive drift,
229   in particular between the reference water samples before and after the three initial internal

230 standards (Fig. 1a, b). The average (SD) drift in reference water during a run was +0.081‰
231 (0.106‰) in δ^{18}O, and +0.62‰ (0.53‰) in δD in the 191 (out of 214) daily runs
232 retained. The drift is also found in the internal standard water analysed at the end of the run
233 compared with the one analysed just after the initial reference waters with an average (SD) drift
234 of +0.069‰ (0.073‰) in δ^{18}O, and +0.43‰ (0.34‰) in δD for the same 191 daily runs subset.
235 These values slightly differ from the drifts for the reference water, which at 99%
236 confidence level is not significant for δ^{18}O, but significant for δD. This may be indicative of
237 errors resulting from linearly adjusting the drift, in particular for the initial standard water
238 samples. This suspicion of a slight non-linearity in the initial drift is reinforced by 7 runs in
239 2020 and 2021 when the three standards were also measured at the end of the run. However,
240 correcting for a non-linear drift is too uncertain, and a correction has not been attempted. The
241 non-linear drift, in addition to being a source of random error (at least 0.02‰ in δ^{18}O and 0.1‰
242 in δD) for individual runs, might also contribute to absolute errors (i.e. in the VSMOW scale)
243 in the range of 0.01‰ in δ^{18}O and 0.05‰ in δD.

245 Occasionally, after the correction of the drift, the value of the last internal standard (last sample
246 port of the run) is shifted for no obvious reason, sometimes by more than 0.10‰ in δ^{18}O from
247 what is expected. This shift might result from a temporary pollution that influences the
248 measurements (organic matter or particles, either left in the cavity of the vaporizer, on the filter
249 or on the salt liner), which can also happen for other sample ports. Often, when this happens,
250 there is also a larger scatter between the different injections, either for this sample or the initial
251 in-house standards. Running the set of samples again or a selection of them, sometimes
252 evidences isotopic shifts that can exceed 0.05‰ in δ^{18} and 0.2‰ in δD. Repeating the analysis
253 helps mitigate this source of uncertainty. But, this has not always been done, except for data
254 sets on which there was a specific emphasis.

256 2.3 Internal standard waters

258 The last large source of uncertainty is the value (in the VSMOW scale) attributed to the internal
259 standards used. On the Isoprime IRMS, most internal standards were extracted from different
260 batches of 'Eau de Paris' (EDP) stored in a tank covered with paraffin, whereas since 2012,
261 three internal standards are regularly extracted from metal tanks where they are kept for up to
262 5-6 years with a slight overpressure of dry air (following Gröning, 2018, TEL Technical Note
263 No. 03). The internal standards have been calibrated using VSMOW and GISP (or GRESP),
264 usually more than once, and some were also sent to other laboratories at different times to
265 independently evaluate their characteristics. Comparisons were done in 2013 and 2014 for three
266 internal LOCEAN standards with 6 laboratories for δ^{18}O and 4 laboratories for δD, which, taken
267 together, did not reveal an average bias larger than 0.01‰ for δ^{18}O or 0.10‰ for δD. However,
268 there seems to be differences for the individual standards (Table 1), with the one at -3.26‰ for
269 δ^{18}O and -21.32‰ for δD presenting an average positive difference of +0.029‰ for δ^{18}O and
270 +0.19‰ for δD, whereas the two other ones present a negative difference (i.e. LOCEAN
271 standards seemed too low) smaller or equal to -0.01‰ for δ^{18}O and -0.19‰ for δD.

273 The next round of comparisons of the LOCEAN internal standards took place between 2019
274 and 2021, with 5 other European laboratories and for two of them, two different setups for δ^{18}O
275 (most of those with IRMS, except for one with a PICARRO L2130-i CRDS). Thus, this
276 includes 7 comparisons for δ^{18}O and 5 for δD. This set of comparisons (Table 1) was done for
277 the three internal standards used in 2019 between 2021, and presents a large scatter between
278 the different laboratories, with standard deviation on the order of 0.055‰ in δ^{18}O and 0.7‰ in
279 δD. As the differences between laboratories are similar for the three internal standards, this

comparison suggests some systematic differences between laboratories. However, the large scatter implies that the average differences found are very uncertain. The differences in δ^{18}O and δD found for the three internal standards used in 2019-2021 range between +0.029‰ in δ^{18}O and +0.21‰ in δD for the less enriched standard to -0.010‰ in δ^{18}O and +0.02 ‰ in δD for the most enriched one, respectively (Table 1). This comparison might indicate that we have a positive bias for two of our recent internal standards, which would also produce a small difference in the response slopes of the Picarro CRDS adopted since 2020. A set of four calibration runs done in November 2021 at LOCEAN with new VSMOW, GRESP as well as three USGS standards with intermediate values confirmed a positive bias on the most negative internal standard (MIX2). This run however did not confirm the average biases on the other internal standards at LOCEAN suggested by Table 1, nor any major slope error. Therefore, the correction of a systematic bias has only been applied on the MIX2 value for analyses since August 2020. For some internal standards, we witnessed larger differences for measurements done in June 2020 after the L2130-i just returned from a cruise and long shipping and storage for more than 9 months. We assume that this anomaly is instrumental, and did not last for a long time, as the anomaly was not reproduced during later tests in August 2020, nor in November 2021.

The two storage methods used successively for internal standard waters were designed to minimize water vapor exchange. It is however possible that small isotopic drifts of the internal standards have taken place with time, due to evaporation or possible oxidation of the tanks (rust was found in one nearly empty tank). As mentioned, based on different comparisons over time, sometimes over remnants of the tank waters, we could verify that these drifts have remained smaller than 0.02‰ in δ^{18}O and 0.1‰ in δD. Finally, standards for the daily runs are temporarily stored, for up to a month, in glass bottles stored at 4°C, which are briefly opened every day to extract water. Through its storage life, this water will slightly exchange with the outside air that penetrates when the bottle is briefly opened. Back of the envelope estimates suggest that the effect should be less than 0.01‰ in δ^{18}O and 0.05‰ in δD, respectively, even after a month.

2.4 Concentration scale

Both oxygen and hydrogen isotope compositions are reported in parts per thousand (‰) on the VSMOW scale. One issue is that we analyse saline samples, while the internal standards are fresh water standards, and the method of analysis has changed over time. There is still a large uncertainty on the correction to be applied to account for the effect of salt on IRMS and CRDS seawater analyses. Here we have applied the corrections provided by Benetti et al. (2017c). Note that in some instances IRMS and CRDS analyses of the same seawater samples may yield similar values. For example, Walker et al. (2016) found very close δ^{18}O values in unadjusted measurements of seawater samples from the same water mass done on different IRMS and CRDS instruments. We have adjusted LOCEAN CRDS and IRMS data on the concentration scale based on the study of Benetti et al. (2017c) as well as on complementary tests with the different wire meshes used more recently and between duplicated IRMS/CRDS samples. The values we report are thus internally consistent, but could present differences with datasets processed in other institutions without this proposed adjustment or with other changes of scale of up to 0.10‰ in δ^{18}O and 0.20‰ in δD, as indicated in Benetti et al. (2017c). We thus expect that adjusted LOCEAN CRDS δ^{18}O data would be higher (more enriched in heavy isotopes) than these other CRDS and more common IRMS data.

2.5 Correction and flagging of samples having probably breathed

329   In regions where there is enough information in the LOCEAN dataset to establish an average
330   relationship between d-excess and salinity (Benetti et al., 2017a), a large breathing of a sample
331   during storage can be detected using its d-excess value, which is then too low compared to the
332   expected relationship. This was recently checked on a set of 10 water samples originating from
333   salinity bottles collected in the surface North Atlantic in 2021 on MV Tukuma Arctica that did
334   not have the usual plastic insert, and thus had evaporated as witnessed by the comparison of
335   their salinity with thermosalinograph records. These samples indeed present higher practical
336   salinity (S), d-excess lower than expected and $\delta^{18}O$ and δD higher than the expected values,
337   estimated by average linear fits of d-excess versus salinity and $\delta^{18}O$ versus S for this region.
338   The average values of the deviations are $\Delta S=+0.29$, $\Delta\delta^{18}O=+0.15$‰; $\Delta\delta D=+0.33$‰, Δd-
339   excess=-0.82‰. The deviations from these expected values present a loose relationship with
340   the deviation in $\delta^{18}O$ ($\Delta\delta^{18}O$) on the order of -20% of the deviation of d-excess (Δd-excess)
341   (Fig. 2). This relationship is close to the one used by Benetti et al. (2017a) based on other data
342   in the Labrador Sea, where $\Delta\delta^{18}O=-1/7$ Δd-excess, $\Delta\delta D=+2$ $\Delta\delta^{18}O$ and Δd-excess = $+0.34$ ΔS.
343   On the other hand, the correlation between Δd-excess and ΔS is not significantly different from
344   0, which might be caused by uncertainties on sampling time causing errors in estimating salinity
345   deviation.
346
347   In cases when breathing was not too large (resulting in an increase of less than $+0.11$‰ in $\delta^{18}O$),
348   we used the deviation from the expected d-excess relationship to S to estimate an adjusted $\delta^{18}O$
349   and δD (Benetti et al., 2017a). When this method is used, $\delta^{18}O$ and δD data are flagged to
350   'probably good' and d-excess to probably bad, as these data are certainly not as accurate as the
351   data with no 'correction', with the adjustment adding an uncertainty on the order of 0.05‰ in
352   ($\delta^{18}O$ and 0.10‰ in δD. For larger suspected evaporation, $\delta^{18}O$ and δD data are not adjusted
353   and flagged as 'probably bad'. Altogether, we have flagged 12.3% of the CRDS-measured
354   samples, most of which (11.3%) correspond to data with anomalously low d-excess and thus
355   suspected evaporation. There is of course also the possibility that for some samples (for 1% of
356   the samples), too low or too high d-excess might just result from an occasional large uncertainty
357   in the analysis.
358
359   We recently tested the effectiveness of applying this adjustment for 32 samples collected during
360   cruise OVIDE2018 (North Atlantic Ocean in 2018; Lherminer, 2018) which were stored in two
361   sets of bottles. One set of bottles was analyzed by CRDS at LOCEAN and the other set by
362   IRMS for $\delta^{18}O$ at Geozentrum Erlangen. Among the 32 LOCEAN samples, 11 show indications
363   of breathing and have been slightly adjusted based on their negative d-excess deviation. The
364   comparison between the 32 LOCEAN and Geozentrum Erlangen isotopic values suggests that
365   the adjustment we applied to 11 of the LOCEAN data results in diminishing from 0.060‰ to
366   0.041‰ the standard deviation of the $\delta^{18}O$ differences between the two sets. The adjustment of
367   the 11 LOCEAN samples also diminished from 0.25‰ to 0.15‰ the standard deviation in the
368   differences between d-excess and d-excess estimated from the d-excess versus S relationship
369   derived for the entire LOCEAN dataset. As a comparison, when the set is restricted to the 21
370   non-adjusted LOCEAN samples, the corresponding standard deviations for the $\delta^{18}O$ differences
371   between LOCEAN and Geozentrum Erlangen values, and d-excess differences to the expected
372   d-excess versus S relationship were 0.043 and 0.14 ‰, respectively. These values are very close
373   to what is found for the set of 32 LOCEAN samples including the 11 adjusted samples,
374   suggesting some homogeneity in the adjusted data set.
375
376   For earlier IRMS analyses at LOCEAN, we base the identification of possible evaporated data
377   on excessive scatter in the $\delta^{18}O$ versus S scatter plots or between successive data compared to
378   what we have previously measured in regions with repeated cruises, and outliers (6%) are

379 flagged as probably bad. The smaller (by half) proportion of flagged IRMS analyses than for
380 the CRDS analyses suggests either that this validation missed some evaporated IRMS samples,
381 or that these earlier data had evaporated less than the more recent ones (some were analyzed
382 sooner after collection), or that the IRMS runs had smaller uncertainties than the latter CRDS
383 runs.
384
385 3. Validation
386 As discussed in section 2, in addition to random errors or to issues related with evaporation of
387 samples, there is the possibility of shifts between subsets of the data, due to the different internal
388 standard waters, methods of processing, adjustment (for CRDS) or conversion from the activity
389 to the concentration scale (for IRMS). We thus need to compare this database with data
390 analyzed in other laboratories, and evaluate time series when the data have been repeated in
391 time at the same location. In particular, the LOCEAN dataset contains a limited number of
392 samples for different cruises in deep-water masses that are unlikely to have experienced much
393 change in their isotopic composition over the last 50 years, due to their weak ventilation and
394 small salinity variability. Examining data in such deep-waters can thus provide a test of
395 consistency between subsets of the LOCEAN data, or relative to other datasets.
396
397 Within the LOCEAN dataset, relevant deep waters have been sampled in different years (in the
398 Southern Indian Ocean (OISO cruises), in the equatorial Atlantic (PIRATA cruises) and in the
399 North Atlantic subpolar gyre (mostly OVIDE cruises), with statistics presented in Table 2.
400 These comparisons on a limited set of cruises, but corresponding to analyses done throughout
401 the 22 last years of the spectrometry platform suggest that internally the δ^{18}O dataset is coherent
402 in time to within 0.035‰ (after an adjustment applied on LOCEAN IRMS data which most of
403 the time was +0.09‰ to adjust to CRDS data). For δD, the period of comparison is more limited
404 with data from Picarro CRDS only since 2010, and the standard error of yearly δD averages is
405 typically on the order of 0.15‰. The comparison also highlights cruises with more noisy data
406 than others. This is for example the case of the 2002 OISO08 IRMS data (without the OISO08
407 data, the mean (standard error) δ^{18}O for subset 1 decreases to +0.078 (0.030) ‰). There are also
408 some suggestions of systematic differences between cruises (for example, for subsets 1-2,
409 OISO29 (2019) samples tend to have lower δ^{18}O and δD values, whereas OISO31 (2021)
410 samples tend to have higher values). However, this is within the uncertainties of the means and
411 is not fully understood. Thus, no further correction is warranted.
412
413 There are δ^{18}O data from a few cruises sampling deep-waters which can be compared with
414 subsets of the LOCEAN data. These together with duplicates sets of samples between
415 LOCEAN and other facilities form the basis for estimating consistency relative to the other data
416 (details in App. A). The different comparisons yielded very varied results. It is often difficult
417 to understand what is the source of the differences, but one commonly suspects choices of
418 protocols, characteristics of the instrument used or internal standards (see also Aoki et al, 2017;
419 Wassenaar et al., 2021). Altogether, although the limited inter-comparisons listed above have
420 a large scatter (the standard deviation in the set of 18 average differences listed in App. A is
421 0.055‰), there is a tendency for LOCEAN δ^{18}O values reported in the concentration scale to
422 be higher (relatively enriched in heavy isotopes). The average of these 18 different comparisons
423 is +0.082‰ with a standard error of 0.016‰ (assuming that the 18 comparisons have the same
424 uncertainty). This average difference happens to be close to the +0.09‰ adjustment that was
425 applied to recent CRDS salty water samples analysed since 2015 at LOCEAN based on Benetti
426 (2017c), an adjustment that was not done on CRDS or IRMS datasets produced in other
427 facilities.
428

429 In summary, these external comparisons, together with the internal consistency tests on the
430 LOCEAN database in a few regions, suggest that the LOCEAN $\delta^{18}O$ dataset are within
431 +0.035‰ absolute accuracy, at least when averaged spatially or in time (Table 2). Individual
432 data have larger uncertainties as discussed before, because of the instrumental and internal
433 standards uncertainty (resulting in a total uncertainty of usually less than 0.05‰ in $\delta^{18}O$) and
434 possible aging/evaporation during collection and storage. We are not able to provide similar
435 comparisons for δD or d-excess, as the database for comparison is much reduced.
436
437 4. The data
438 4.1 Data distribution
439 Fig. 3 presents the spatial distribution of the LOCEAN-analyzed data close to the surface, with
440 the largest data collection being in the North Atlantic (Fig. 3a) (in particular, with OVIDE
441 cruises since 2002 and the SURATLANT ship of opportunity dataset since 2011), the tropical
442 Atlantic (in particular, the EGEE and PIRATA cruises since 2005), and the South Indian Ocean
443 (Fig. 3b) (OISO cruises since 1998).
444
445 Table 3 reports the number of valid data points by depth range, which indicates that the
446 emphasis in this set has been on near surface data (58% of the $\delta^{18}O$ data above 40m depth, with
447 13% between 40 and 200m depth, and only 12% at 1000m or deeper). There is less valid δD
448 than $\delta^{18}O$ data, the difference corresponding to IRMS-measured data, which correspond to 25%
449 of the total number of water samples in the database. There is even less valid d-excess than δD
450 (by 10%), the difference corresponding to samples for which an adjustment for slight
451 evaporation was done on $\delta^{18}O$ and δD data. The database contains fewer deep samples since
452 the transition to CRDS than before, because of a recent emphasis of sampling the upper ocean.
453
454 4.2 Time series
455 We illustrate the dataset with time series of June (or July) data between 50° and 55°N in the
456 eastern North Atlantic subpolar gyre (NASPG) collected mostly during the OVIDE cruises
457 (Fig. 4). This scatter plot of cruise-averaged S and $\delta^{18}O$ indicates a near alignment of the values.
458 It is striking that the strongest negative (fresher/lighter) anomalies in 2016 fit rather well on the
459 regression line (in red) for water samples in the southwestern NASPG. This regression line is
460 derived from data from the 47–55°N, 30-49°W region, excluding very low salinity data from
461 seasonal sea ice melt or from shelf waters, and is very similar to the distribution in Frew et al.
462 (2000). Thus, this reinforces the hypothesis of Holliday et al. (2020) that the strong freshening
463 present in the eastern subpolar gyre in 2016 originated from the transport of Arctic freshwater
464 from the western boundary current into the eastern basins, and not from local rainfall, which
465 would have likely resulted in higher $\delta^{18}O$ at the same 'low' salinity such as depicted by the
466 black line (Frew et al., 2000; C. Risi, pers. comm., 2021).
467
468 The SURATLANT surveys provided a seasonal sampling of water isotopes between late 2011
469 and 2019 along the western flank of the Reykjanes Ridge in the central part of the gyre (53-
470 56°N/38°-44°W). Annual summaries of these data are provided on Fig. 5a. There is less
471 alignment of the interannual values on the average southwestern NASPG linear regression line
472 than for the OVIDE surveys (Fig. 4). However, there is some aliasing of the seasonal cycle in
473 the annual averages (see Reverdin et al., 2018b), which contributes to the scatter, as well as
474 noise on the data, and natural variability. On this plot the freshest year appears to be 2017, in
475 agreement with an analysis using a much more complete salinity dataset (Reverdin et al.,
476 2018a). 2017 is also one of the lighter $\delta^{18}O$ years. The corresponding d-excess versus S diagram
477 (Fig. 5b) presents yearly anomalies that are fairly aligned with the average regression between

southwestern NASPG d-excess and salinity data. Error bars are large, but nevertheless, low salinity waters exhibit high d-excess, as described in Benetti et al. (2017a, b).

5. Data availability:

The dataset described is version V2 at https://doi.org/10.17882/71186 (Waterisotopes-CISE-LOCEAN, 2021).

6. Conclusions

Instrumental uncertainty on individual data in this dataset is as low as 0.03‰, in $\delta^{18}O$ and 0.15‰ in δD for most runs, with occasional much larger uncertainties. One needs to add to that the uncertainties on the internal standards that are used to convert measured values into the VSMOW scale. Different comparisons suggest that the internal standard values have almost always remained defined within at most 0.03‰ for $\delta^{18}O$ and 0.2‰ for δD, since 2012. There was however a short-term larger difference found for the most negative standard (equal to 0.1‰ for $\delta^{18}O$), most likely related to the readjustment of the instrument to laboratory conditions in May 2021. When using the CRDS Picarro L2130-i, we also found periods with quite uncertain analyses, in particular due to salt or particle deposit in the vaporizer or filters. These samples could often be run again afterwards to reach lower resulting uncertainty.

Finally, there is the issue of possible evaporation during collection and storage. When the analysis is done on a CRDS, we are usually able to detect possible biases larger than 0.05‰ in $\delta^{18}O$, by comparing d-excess with the expected d-excess derived from regional d-excess-S linear relationships. Attempts were made here to correct $\delta^{18}O$ and δD when the resulting uncertainty does not exceed 0.05‰ and 0.1‰, respectively. In particular this was done for some OISO cruise samples which were analysed many years after collection, or in the case of faulty caps being used, or caps that were not properly closed and wrapped with parafilm. This is certainly a strong source of quality loss for part of the database, and 'small' effects may have remained undetected.

Possible long-term drifts due to changes in internal standards, storage, instrumentation and protocols are difficult to estimate. This is done here by checking the consistency of different subsets of the database, for instance when time series can be obtained (such as in the southern Indian Ocean or North Atlantic subpolar gyre), or by comparison with duplicate data analysed in other laboratories, or with other datasets in deep regions commonly sampled. These comparisons are encouraging. On one hand, they suggest that the internal consistency in the database is usually within an uncertainty of 0.03‰ for $\delta^{18}O$ and 0.15‰ for δD. On the other hand, although other datasets sometimes differ by much more with a large scatter between the 18 comparisons (with a standard deviation of 0.055‰ for $\delta^{18}O$), the average difference (+0.082‰) found with them is close to the adjustment that is applied to the LOCEAN data to report them on the concentration scale (+0.09‰ for $\delta^{18}O$ analyzed with a salt liner since 2015). Of course, there is still the possibility of errors and biases in subsets that could not be compared in a similar way, such as surface samples collected from ships of opportunity or sailing vessels in the tropics, that could result from different handling of the samples during collection and more uncertain storage conditions. There are also small errors originating from memory effects in the Picarro CRDS runs that could be better corrected and taken into account (Vallet-Coulomb et al., 2021).

We also illustrated the possibility of using this dataset to investigate ocean variability. Of course, the interest of a data archive is to merge different institutes datasets such as this one, while retaining a similar accuracy. This was attempted in the Global Seawater Oxygen-18

528 Database at GISS (Schmidt et al., 1999), although biases between subsets of this mostly $\delta^{18}O$
529 dataset remain at a level that makes the overall analysis of variability difficult to carry. The few
530 comparisons we could do suggest that differences with other datasets are at times large. The
531 effort to correctly adjust for these differences and produce a larger coherent archive is required
532 to get full use of the data collected. There is still a need of more and better calibrated seawater
533 isotope data to reconstruct tropical hydroclimate variability, such as formulated for the tropical
534 coral archives by PAGES CoralHydro2k Project, or for high latitude studies of the various
535 sources of freshwater in the ocean, including continental runoff, sea ice, iceberg melt and air-
536 sea exchanges.
537
538 Appendix A: Comparisons of LOCEAN data with other isotopic data
539 This includes on one hand comparisons with data of other cruises, in areas where we expect
540 variability to have been weak, such as in the deep ocean, and on the other hand, considering
541 duplicate sets of samples analysed in different institution.
542
543 Akhoudas et al. (2021) used the first approach in the deep Weddell Sea, comparing the
544 LOCEAN 2017 Wapiti cruise data with data from other cruises over a fairly large range of
545 neutral density surfaces. They identified a cruise whose $\delta^{18}O$ values were lower by 0.13‰ than
546 at LOCEAN, as well as datasets that fit the Wapiti cruise values to within the data uncertainties
547 (for example, from ANT-X12 cruise on RV Polarstern in 1995). Another water mass which can
548 be used for comparison is the near - bottom waters in Fram Strait (below 2000m), which are
549 either originating from the Arctic Ocean, or recirculating from the Greenland Sea. This water
550 mass is regularly sampled, and has not been strongly ventilated recently. In 1998-2015 during
551 German-led cruises, these waters presented an average $\delta^{18}O$ value close to +0.28‰ (after
552 removing suspiciously high data of a cruise in 2011 and large positive outliers in 2012; Paul
553 Dodd, personal communication). The LOCEAN database contains seven $\delta^{18}O$ samples close to
554 the bottom across Fram Strait from MSM76 cruise on RV Maria S Merian in 2018, with average
555 (SD) value close to +0.395 (0.035) ‰, thus averaging higher by 0.115‰ than the other set in
556 1998-2015.
557

558 We extracted individual profiles from the GISS Global Seawater Oxygen-18 Database
559 (Schmidt et al., 1999) that can be compared with the LOCEAN station data, in deep and old
560 water masses. In the southern Indian Ocean, for example numerous profiles collected during
561 1993-1994 cruises (CIVA1 (Archambeau et al., 1998), ADOX1, SWINDEX, ADOX2)
562 suggest that LOCEAN $\delta^{18}O$ in the deep layers are higher by 0.10‰ to 0.17‰ depending on
563 the cruise. There is also one GEOSECS 1978 station with a single deep value within 0.01‰
564 of close-by OISO stations, as well as some 1984 (INDIVAT1) and 1996 (CIVA2) station data
565 with larger uncertainties that indicate higher LOCEAN $\delta^{18}O$ values by 0.15‰ to 0.22‰,
566 depending on how outliers are identified and removed.
567
568 In the North Atlantic, there are data from three cruises that can be directly compared with
569 LOCEAN data, focusing on deep waters with T-S properties close to the ones of the
570 LOCEAN dataset. Comparison with one GEOSECS 1972 station south of Greenland suggests
571 higher $\delta^{18}O$ LOCEAN values by ~ 0.060‰ (there is a small salinity shift between the two
572 profiles which required to adjust the LOCEAN $\delta^{18}O$ value to the same salinity based on the
573 average $\delta^{18}O$-S relationship). Data of 4 stations of the CONVEX1991 cruise (Frew et al.,
574 2000) indicate higher $\delta^{18}O$ in LOCEAN dataset by ~ 0.090‰ (after adjustment done to
575 consider small salinity differences). On the other hand, data close to the North East Atlantic
576 deep-water layer from stations collected in June 1995 in the southern Labrador Sea
577 (Khatiwala et al., 1999) do not show a significant difference with LOCEAN stations closer to
578 south Greenland (southern Irminger Sea) at a similar salinity. In the equatorial Atlantic there
579 are deep data of two GEOSECS stations collected in 10/1972 and 2/1973 that can be
580 compared with the LOCEAN data (mostly near 1000-2000m depth). These limited
581 comparisons (often at large distance, but at a similar salinity) suggest that LOCEAN values
582 are larger than the GEOSECS $\delta^{18}O$ by 0.055‰.
583
584 Finally, there are a few instances of seawater samples that have been duplicated and shared
585 with other laboratories. Some of these in 2013-2014 have been used to validate how to convert
586 IRMS or CRDS measurements into the concentration scale, with or without distillation (Benetti
587 et al, 2017c), that we will not include here, and that suggested a scatter in the comparisons with
588 different IRMS laboratories for natural or artificial seawater samples often on the order of
589 0.10‰. More recently, 18 samples of the WAPITI2017 cruise were duplicated with analyses
590 both at LOCEAN and at the British Geological Survey stable isotope facility (BGS), which
591 indicated lower LOCEAN $\delta^{18}O$ averaging -0.09‰ (SD = 0.035 ‰) (Akhoudas et al., 2021). In
592 the same region, a small set of 11 samples was duplicated in 2020 with Hokkaido University,
593 which suggests that LOCEAN $\delta^{18}O$ values are higher by +0.139 ‰ with a SD of 0.019 ‰
594 (Shigeru Aoki, pers. comm., 2021). Another set of 137 samples was duplicated in 2017 in the
595 Southern Ocean from the Antarctic Circumnavigation Experiment cruise with samples analyzed
596 at BGS (Haumann et al., 2019), which yielded an average difference of +0.004 (SD = 0.055
597 ‰).
598
599 There have also been duplicates of LOCEAN samples during OVIDE cruises in 2010, 2016 and
600 2018 analysed in different facilities (Antje Voelker, pers. comm., 2021), which suggested
601 diverse average offsets for the different years. In particular for 2016 samples close to 2500m,
602 LOCEAN values average higher by +0.035‰, whereas in 2018, the average difference is closer
603 to +0.07‰, but with a few stations at the north-western end of the section in Irminger sea with
604 differences on the order of +0.02‰.
605
606 Author contribution:

662
663
664

665 References:
666 Akhoudas, C., Sallée, J.-B., Reverdin, G., Aloisi, G., Benetti, M., Vignes, L., and Gelado. M.:
667 Ice-shelf basal melt and influence on dense water outflow in the southern Weddell Sea, J.
668 Geophys. Res.: Oceans, 125, e2019JC015710, doi:10.1029/2019JC015710, 2020.
669 Akhoudas, C. H., Sallée, J.B., Reverdin, G., Meredith, M. P., Naveira Garabato, A., Haumann,
670 F. A., Jullion, L., Aloisi, G., Benetti, M., Leng, M. L., Arrowsmith, C. : Ventilation of the abyss
671 in the Atlantic sector of the Southern Ocean, Nature Sci Repc 11**,** 16733 (2021),
672 https://doi.org/10.1038/s41598-021-95949-w, 2021.
673 Aoki, S., Kobayashi, R. , Rintoul, S. R., Tamura, T., and Kusahara, K.: Changes in water
674 properties and flow regime on the continental shelf off the Adélie/George V Land coast,
675 East Antarctica, after glacier tongue calving, J. Geophys. Res.: Oceans, 122 (8), 6277 –
676 6294, 2017.
677 Archambeau A.S., Pierre C., Poisson A., Schauer, B.: Distribution of CFC-12, Oxygen and
678 carbon stable isotopes in the Water masses of the Southern Ocean at 30°E from Africa to
679 Antarctica, J. Mar. Sys., 17, 25-38, 1998.

680 Benetti, M., Reverdin, G., Pierre, C., Khatiwala, S., Tournadre, B., Olafsdottir, S., and
681 Naamar, A.: Variability of sea ice melt and meteoric water input in the surface Labrador
682 Current off Newfoundland., J. Geophys. Res. Oceans, 121, 2841–2855,
683 doi:10.1002/2015JC011302, 2015.

684 Benetti, M., Reverdin, G., Yashayaev, I., Holliday, N.P., Tynuan, E., Torres-Valdes, S.,
685 Lherminier, P., Tréguer, P., Sarthou, G., and Lique, C.: Composition of freshwater in the
686 spring of 2014 on the southern Labrador shelf and slope. J. Geophys. Res.: Oceans, 122,
687 1102-1121, doi: 10.1002/2016JC012244, 2017a.

688 Benetti, M., Reverdin, G., Aloisi, G., and Sveinbjörnsdóttir, A.: Stable isotopes in surface
689 waters of the Atlantic Ocean: indicators of ocean-atmosphere water fluxes and oceanic
690 mixing processes, J. Geophys. Res. Oceans, doi:10.1002/2017JC012712, 2017b.

691 Benetti, M., Sveinbjörnsdottir, A.E., Leng, M.J., Arrowsmith, C., Debondt, K., Fripiat, F., and
692 Aloisi, G.: Inter-comparison of salt effect correction for $\delta^{18}O$ and $\delta^{2}H$ measurements in
693 seawater by CRDS and IRMS using the gas-H_2O equilibration method, Mar. Chem., 194,
694 114–123, Doi :10.1016/j.marchem.2017.05.010, 2017c.

695 Benetti, M., Reverdin, G., Clarke, J. S.,Tynan, E., Holliday, N. P., Torres-Valdes, S.,
696 Lherminier, P., Yashayaev, I.: Sources and distribution of fresh water around Cape Farewell in
697 2014, J. Geophys. Res., doi:10.1029/2019JC015080, 2019.
698 Bigg, G.R., and Rohling, E.J.: An oxygen isotope dataset for marine water, J. Geophys. Res.
699 Atmos., 105, 8527-8536, doi:10.1029/2000JC900005, 1999.
700 Craig, H., and Gordon, L.I.: Deuterium and oxygen18 variations in the ocean and marine
701 atmosphere, In:Tongiogi,E.(Ed.),Proc. Stable Isotopes in Oceanographic Studies and
702 Paleotemperatures, pp.9–130 (V.Lishie e F., Pisa), 1965.
703 Frew, R., Dennis, P.F., Heywood, K., Meredith, M.P., and Boswell, S.M.: The oxygen isotope
704 composition of water masses in the Northern North Atlantic, Deep-Sea Res. I, 47, 2265-2286,
705 doi:10.1016/S0967-0637(00)00023-6, 2000.
706 Gröning, M.: Stable Isotope Internal Laboratory Water Standards: Preparation, Calibration and
707 Storage., TEL Technical Note No. 03, (revised from IHL Technical Procedure Note No.43,
708 Tanweer et al., as of May 2009), 2018.
709 Haumann, F. A., K. Leonard, M. P. Meredith, C. Arrowsmith, I. V. Gorodetskaya, J. Hutchings,
710 M. Lehning, M. J. Leng, S. Stammerjohn, M. Tsukernik, Y. Weber, 2019. Seawater stable
711 isotope sample measurements from the Antarctic Circumnavigation Expedition (ACE)
712 (Version 1.0) [Data set]. *Zenodo*. doi:10.5281/zenodo.1494915.

713 Holliday, N.P., M. Bersch, B. Berx, L. Chafik, S. Cunningham, C. Florindo-López, H. Hátún, W.
714 Johns, S.A. Josey, K. M. H. Larsen, S. Mulet, M. Oltmanns, G. Reverdin, T. Rossby, V. Thierry,
715 H.Valdimarsson, I. Yashayaev, 2020. Ocean circulation changes cause the largest freshening
716 event for 20 years in the eastern subpolar North Atlantic. Nature Communications, 11, DOI:
717 10.1038/s41467-020-14474-yKhatiwala, S. P., Fairbanks, R. G., and Houghton, R.
718 W.:Freshwater sources to the coastal ocean off northeastern North America: Evidence from
719 $H_2^{18}O/H_2^{16}O$, J. Geophys.Res. 104: 18241–18255, doi:10.1029/1999JC900155, 1999.
720 Lherminier, P., 2018: OVIDE 2018 cruise, RV Thalassa,
721 https://doi.org/10.17600/18000510.
722 Lis, G., Wassenaar, L., and Hendry, M.: High-precision laser spectroscopy D/H and 18O/16O
723 measurements of microliter natural water samples, Analytical chemistry 80(1), 287-293,
724 2008.
725 Östlund, H.G., Craig, H., Broecker, W. S., and Spenser, D.: GEOSECS Atlantic, Pacific and
726 Indian Ocean Expeditions: Shore based Data and Graphics,Technical Report, National
727 Science Foundation, Washington, DC, p.220, 1987.
728 Reverdin G, Alory, G., Diverres, D., Bringas, F., Goni, G., Heilmann, L., Chafik, L., Szekely,
729 T., and Friedman, A.R.: North Atlantic subpolar gyre along predetermined ship tracks since
730 1993: a monthly data set of surface temperature, salinity, and density, Earth Syst. Sci. Data
731 10: 1403-1415, doi:10.5194/essd-10-1403-2018, 2018a.
732 Reverdin, G., Metzl, N., Olafsdottir, S., Racapé, V., Takahashi, T., Benetti, M.,
733 Valdimarsson, H., Benoit-Cattin, A., Danielsen, M., Fin, J., Naamar, A., Pierrot, D., Sullivan,
734 K., Bringas, F., and Goni, G. : SURATLANT: a 1993–2017 surface sampling in the central
735 part of the North Atlantic subpolar gyre, Earth Syst. Sci. Data, 10, 1901-1924,
736 doi:10.5194/essd-10-1901-2018, 2018b.
737 Reverdin, G., Metzl, N.., Reynaud, T., Poli, P., Griboval, Y. : L'Exploreur OceanoScientific
738 "Boogaloo" - Une campagne péri-Antarctique, 26/01/2017 - 04/04/2017, La Météorologie,
739 April 2020, doi :10.1002/2016JC012244, 2019.
740 Schmidt, G.A.: Error analysis of paleosalinity calculations, Paleoceanography , 14, 422-
741 429, doi:10.1029/1999PA900008, 1999.
742 Schmidt, G.A., Bigg, G.R., and Rohling E.J.: Global Seawater Oxygen-18 Database – Data,
743 GISS, http://www.giss.nasa.gov/data/o18data/, 1999.
744 Skrzypek, G., and Ford, D.: Stable isotope analysis of saline water samples on a cavity
745 ringdown spectroscopy instrument, Environ. Sci. Technol., 48, 2827-2834,
746 doi:10.1021/es4049412, 2014.
747 Stevens et al : EUREC^{4}A , Earth Sys. Sci. Data, 13, 4067–4119, https://doi.org/10.5194/essd-13-
748 4067-2021, 2021.
749 Vallet-Coulomb C., Couapel M., and Sonzogni C.: Improving memory effect correction to
750 achieve high-precision analysis of delta O-17, delta O-18, delta H-2, O-17-excess and d-
751 excess in water using cavity ring-down laser spectroscopy, Rapid Comm. In Mass Spectr.,
752 35 (14), p. e9108 [16 p.] ISSN 0951-4198, 2021.
753 Voelker, A.H., Colman, A. , Olack, G., and Waniek, J.: Oxygen and hydrogen isotope
754 signatures of northeast Atlantic water masses, Deep Sea Res. II, 116,
755 doi:10.1016/j.dsr2.2014.11.006, 2015.
756 Walker, S.A., Azetsu-Scott, K., Normandeau, C., Kelley, D.E., Friedrich, R., Newton, R.,
757 Schlosser, V, McKay, J.L., Abdi, W., Kerrigan, E., Craig, S.E., and Wallace, D.W.R.: A
758 comparison of cavity ring-down spectroscopy (CRDS) and isotope ratio mass
759 spectrometry (IRMS), Limnology and Oceanogr.: Meth., doi: 10.1002/lom3.10067, 2016.
760 Wassenaar, L.I., Terzer-Wassmuth, S., and Douence, C.: Progress and challenges in dual-
761 and triple-isotope ($\delta^{18}O$, δ^2H, $\Delta^{17}O$) analyses of environmental waters: an international

762 assessment of laboratory performance, Rap. Comm. In Mass Spectrom., in Press,
763 doi:10.1002/rcm.9193, 2021.
764 Waterisotopes-CISE-LOCEAN, Water isotopes of seawater analyzed since 1998 at
765 LOCEAN, SEANOE. https://doi.org/10.17882/71186, 2021.
766 Xu, X., Werner, M., Butzin, M., and Lohmann, G.: Water isotope variations in the global
767 ocean model MPI-OM, Geosci. Model Dev., 5,809-818, doi:10.5194/gmd-5-809-2012,
768 2012.
769
770
771

772   Table 1

773   Comparison of standards measured at LOCEAN and in other laboratories (in ‰). The
774   laboratories in the 2013-2014 comparisons took place at LSCE (France), LDEO (Columbia
775   University, USA), NIOZ (Netherlands), VRIJE (Brussels, Belgium), Dalhousie Univ
776   (Dahlousie, Canada), BGS (Nottingham, UK), U. Ottawa (Ottawa, Canada), and in 2018-2019,
777   at GeoZentrum NordBayern (Erlangen, Germany), AWI (Bremerhaven, Germany), U. Kiel
778   (Kiel, Germany), LSCE (France), U. Bergen (Bergen, Norway).

Date	Internal Standard	LOCEAN $\delta^{18}O$ ‰	LOCEAN δD ‰	$\delta^{18}O$ deviation ‰	Nber of $\delta^{18}O$ lab settings	δD deviation ‰	Nber of δD lab settings
2013-2014	EDP	-6.610	-44.30	-0.010	6	-0.19	4
2013-2014	MIX	-3.260	-21.32	+0.029	6	+0.19	4
2013-2014	KONA	-0.050	+0.46	-0.007	6	-0.18	4
2019-2021	MIX2	-2.610	-17.93	+0.029	7	+0.21	5
2019-2021	BERING	-0.805	-4.56	+0.028	7	+0.19	5
2019-2021	KONA3	+1.220	+3.40	-0.010	7	+0.02	5

779
780

781 Table 2
782 Comparison of LOCEAN annually-averaged data in a few selected deep-water masses which
783 exhibit little variability in their salinity, and have likely not been recently ventilated. S, $\delta^{18}O$,
784 δD and d-excess values are first averaged for each year. The values reported are the mean and
785 standard deviations of these yearly averages. The number of years (N years) refers to the $\delta^{18}O$
786 data.
787 1: OISO cruises (1998 to 2021) near 1000-1500m in South Indian Ocean Antarctic sector of
788 the Southern Ocean (50°S-58°S) (1998*, 2002*, and most years since 2010)
789 2: OISO cruises (1998 to 2021) near 2000m in the western South Indian Ocean subtropical gyre
790 (1998*, 2002*, and most years since 2010)
791 3: PIRATA and EGEE cruises (2005-2021) near 1000m in eastern equatorial Atlantic (2005*,
792 2006*, 2007*, 2015, 2020, 2021)
793 4: OVIDE and RREX2017 data between 2000m and 3500m in eastern North Atlantic subpolar
794 gyre (data in 2002*, 2016, 2017, 2018, 2021)
795

Cruise set	1	2	3	4
N years	13	9	6	5
S	34.710 (0.013)	34.695 (0.005)	34.615 (0.010)	34.936 (0.010)
$\delta^{18}O$ (‰)	+0.095 (0.035)	+0.085 (0.035)	+0.150 (0.020)	+0.287 (0.030)
δD (‰)	-0.25 (0.13)	-0.29 (0.10)	+0.24 (0.15)**	+1.18 (0.20)
d-excess (‰)	-0.80 (0.15)	-1.03 (0.19)	-0.81 (0.0)**	-1.05 (0.10)

796 * IRMS estimates for $\delta^{18}O$ only.
797 ** only two years
798
799

800 Table 3
801 Number of valid seawater isotopic data by depth range in Waterisotopes-CISE-LOCEAN
802 (2021, version V2) (a total of 7595 valid data for $\delta^{18}O$ out of 7703 data entries)
803

Depth range (m)	$\delta^{18}O$ (‰)	δD (‰)	d-excess (‰)
0-40	4517	3416	3180
40-199	1029	716	625
200-999	1245	1029	919
> 999	804	539	465
total	7595	5700	5189

804
805
806
807

808   Figure captions
809   Figure 1: A typical run (on 2/08 2021) of 19 samples using three internal standards and
810   KonaDeep-water samples (left for δ^{18}O and right for δD). Top panels (a, b): the deviations of
811   isotopic values (‰) of internal standards (in blue) and of the KonaDeep-water samples (in red)
812   relative to their expected values (horizontal axis is sample number). Error bars are the standard
813   deviation of the different injections, and the vertical scale is arbitrary set so that 0 corresponds
814   to KonaDeep sample 6 (after the three internal standards). The lower panels (c, d) present the
815   values obtained after adjusting for the drifts identified with the KonaDeep-water samples
816   through the run.
817
818   Figure 2: Scatter diagram of the deviation of δ^{18}O (‰) versus the deviation of d-excess (‰) for
819   a set of samples extracted from salinity bottles with no plastic inserts that had evaporated (2021,
820   mostly from MV Tukuma in the North Atlantic). The deviations are estimated by subtracting
821   from the isotopic data the isotopic value estimated as a function of practical salinity, based on
822   the other regional data. The error bars on each sample are the standard deviation between the
823   different injections and assuming that the standard deviation of δ^{18}O and δD are independent
824   when estimating d-excess. The red line is the regression used in Benetti et al. (2016).
825
826   Figure 3: Maps which include most of the near-surface δ^{18}O data in the LOCEAN archive (color
827   scale δ^{18}O in ‰). (3a) Arctic and Atlantic oceans; (3b) other oceanic regions.
828
829   Figure 4: Scatter plot of cruise averages of near surface (upper 100-m) δ^{18}O (‰) versus
830   practical salinity in the Iceland Basin, close to the NAC fronts. The bars indicate the standard
831   deviation between the individual data that are averaged. Notice the fresher and isotopically
832   lighter data from the BOCATS (OVIDE transect) cruise in 2016. The red line corresponds to
833   the average linear relationship in the south-western NA SPG (SURATLANT dataset within 47–
834   55°N and 30-49°W, with practical salinity between 33.1 and 35.5), whereas the black line
835   reports the slope expected from mixing with local rainfall end-member.
836
837   Figure 5: Scatter plots in the southern Irminger Sea/NASPG of annually averaged
838   SURATLANT surveys data. (a) presents δ^{18}O (‰) versus practical salinity, whereas (b)
839   presents d-excess (‰) versus practical salinity. The bars indicate the standard deviation
840   between the individual data that are averaged. The red lines correspond to the average linear
841   relationships in the SURATLANT dataset within 47–55°N and 30-49°W, with salinity between
842   33.1 and 35.5 (see Reverdin et al., 2018b), the red line on the left panel, being the same as on
843   Fig. 4.
844
845
846
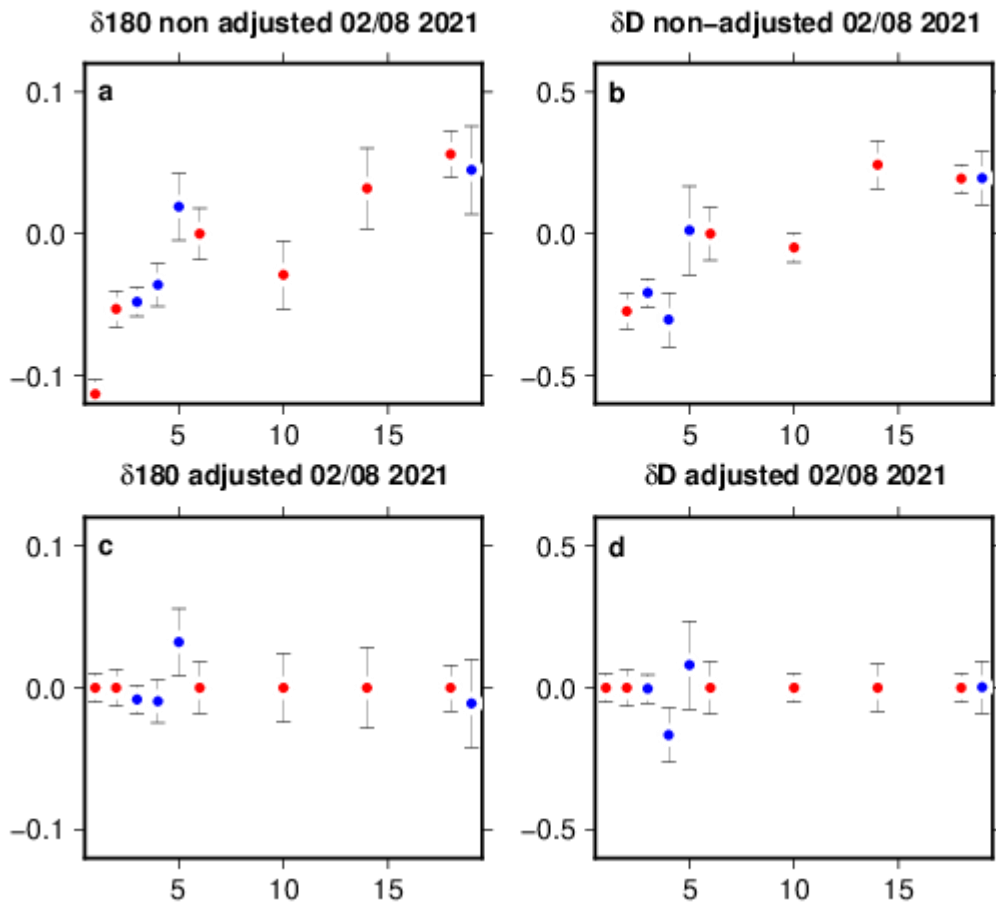
848
849 Figure 1: A typical run (on 2/08 2021) of 19 samples using three internal standards and
850 KonaDeep-water samples (left for $\delta^{18}O$ and right for δD). Top panels (a, b): the deviations of
851 isotopic values (‰) of internal standards (in blue) and of the KonaDeep-water samples (in
852 red) relative to their expected values (horizontal axis is sample number). Error bars are the
853 standard deviation of the different injections, and the vertical scale is arbitrary set so that 0
854 corresponds to KonaDeep sample 6 (after the three internal standards). The lower panels (c, d)
855 present the values obtained after adjusting for the drifts identified with the KonaDeep-water
856 samples through the run.
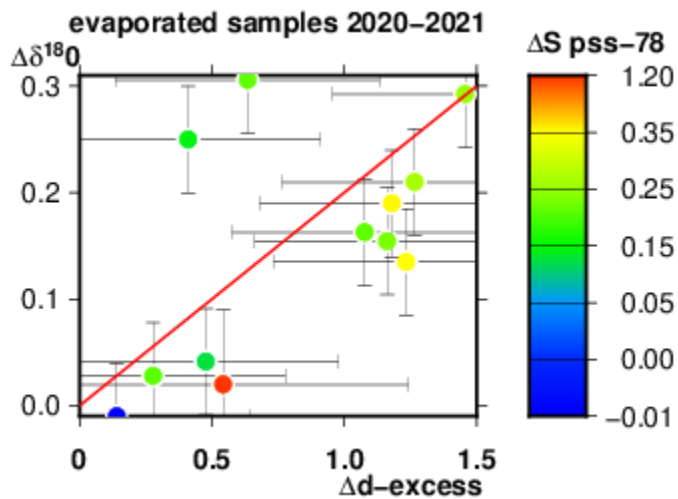
Figure 2: Scatter diagram of the deviation of δ^{18}O (‰) versus the deviation of d-excess (‰) for a set of samples extracted from salinity bottles with no plastic inserts that had evaporated (2021, mostly from MV Tukuma Arctica in the North Atlantic). The deviations are estimated by subtracting from the isotopic data the isotopic value estimated as a function of practical salinity, based on the other regional data. The error bars on each sample are the standard deviation between the different injections and assuming that the standard deviation of δ^{18}O and δD are independent when estimating d-excess. The red line is the regression used in Benetti et al. (2016).
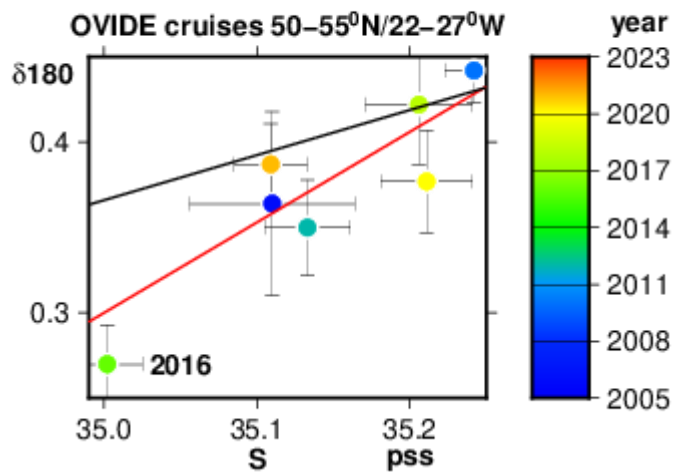
867
868
869

870
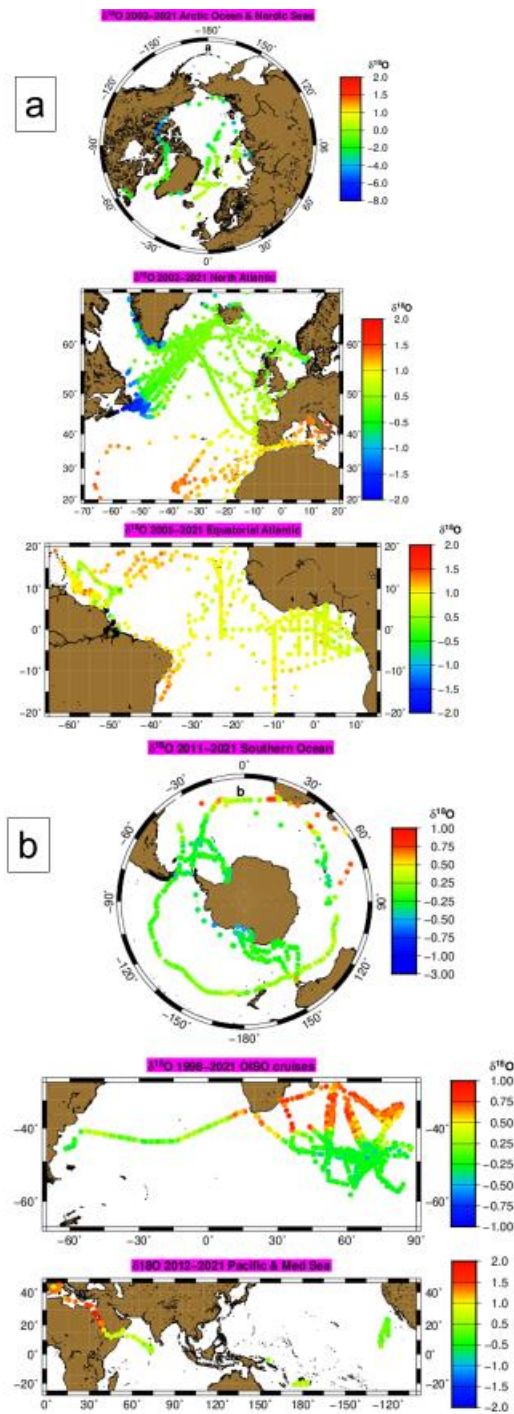
871
872 Figure 3: Maps which include most of the near-surface δ^{18}O data in the LOCEAN archive (color
873 scale δ^{18}O in ‰). (3a) Arctic and Atlantic oceans; (3b) other oceanic regions.
874

877 Figure 4: Scatter plot of cruise averages of near surface (upper 100-m) $\delta^{18}O$ (‰) versus
878 practical salinity in the Iceland Basin, close to the NAC fronts. The bars indicate the standard
879 deviation between the individual data that are averaged. Notice the fresher and isotopically
880 lighter data from the BOCATS (OVIDE transect) cruise in 2016. The red line corresponds to
881 the average linear relationship in the south-western NA SPG (SURATLANT dataset within
882 47–55°N and 30-49°W, with practical salinity between 33.1 and 35.5), whereas the black line
883 reports the slope expected from mixing with local rainfall end-member.

884
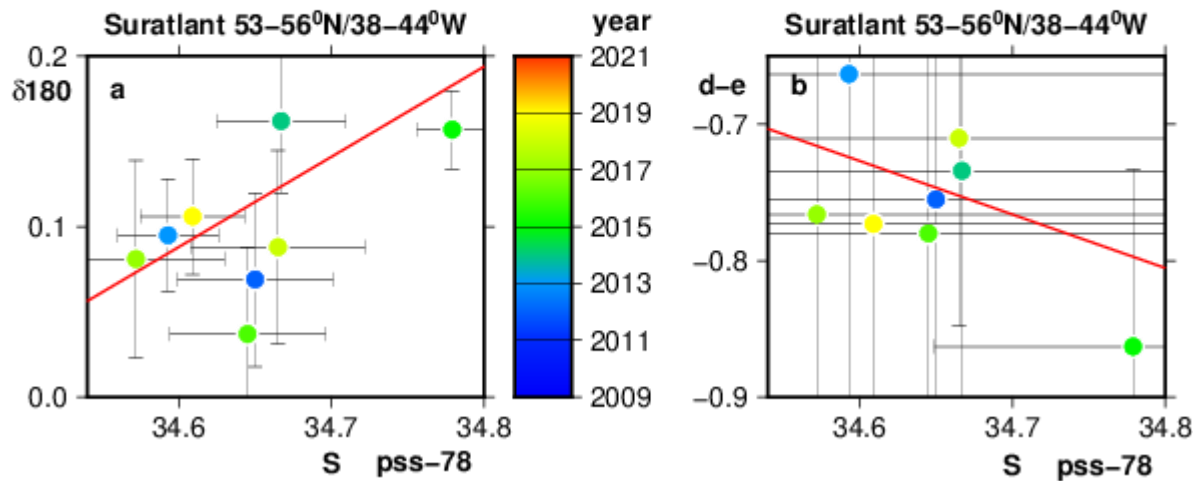
885
886 Figure 5: Scatter plots in the southern Irminger Sea/NASPG of annually averaged
887 SURATLANT surveys data. (a) presents $\delta^{18}O$ (‰) versus practical salinity, whereas (b)
888 presents d-excess (‰) versus practical salinity. The bars indicate the standard deviation
889 between the individual data that are averaged. The red lines correspond to the average linear
890 relationships in the SURATLANT dataset within 47–55°N and 30-49°W, with salinity between
891 33.1 and 35.5 (see Reverdin et al., 2018b), the red line on the left panel, being the same as on
892 Fig. 4.