An Expanded Batch-to-Batch Correction for IAPSO Standard Seawater

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ABSTRACT

We expanded the batch-to-batch offsets of The International Association for the Physical Sciences of the Oceans (IAPSO) Standard Seawater (SSW) batches P145–P163 by intercomparison measurements using salinometers. On the basis of our results, we recommend using the correction factors instead of the offsets to correct the batch-to-batch differences, especially for salinity data outside the range of 30–40 g kg^{−1}. We evaluated the expanded batch-to-batch correction factors by applying them to time series salinity data collected in the northwestern North Pacific Ocean and found that they are effective for detecting recent freshening ($-0.6 \pm 0.1 \times 10^{-3}$ g kg^{−1} decade^{−1}) in the deep North Pacific, which might be related to a reduction of the formation rate of Antarctic Bottom Water. We also evaluated the SSW linearity pack by applying the batch-to-batch correction factors. Linearity errors of the salinometers estimated from decade resistance substituters were consistent with the results of the linearity pack measurements. To correct the linearity errors of a salinometer, it might be suitable to use the more detailed distribution of those estimated from the decade resistance substituter than the linearity pack measurements. Since the cause of large batch-to-batch differences is still unclear, a reference seawater that is more robust and stable than SSW might be necessary to establish a high-level of international comparability of salinity measurements; the Multiparametric Standard Seawater (MSSW) currently under development might be a candidate for such reference seawater, because MSSW is expected to be more stable than SSW not only in practical salinity but also in absolute salinity.

1. Introduction

The salinity of the ocean is an important indicator of Earth's climate change. For example, the Southern Ocean has freshened and warmed over the past several decades primarily as a result of human-induced greenhouse gas increases (Swart et al. 2018). Swart

et al. (2018) concluded that the primary changes of the freshening result from changes in precipitation and the northward advection of freshwater by sea ice. The freshening substantially increases the buoyancy of the seawater and perhaps reduces the formation rate of Antarctic Bottom Water (Purkey et al. 2019). Purkey et al. (2019) also observed an infusion of freshwater propagating along the pathway of the bottom water as

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it moves northward from Antarctica. Monitoring long-term changes in the deep-sea environment, such as freshening of abyssal waters, requires salinity measurements of the highest possible quality (Levin et al. 2019).

To establish comparability of salinity data, a bottled standard reference material called The International Association for the Physical Sciences of the Oceans (IAPSO) Standard Seawater (SSW) has been used worldwide for more than 40 years (Culkin and Ridout 1998). However, there is a fundamental problem with seawater salinity measurements: a lack of traceability to the International System of Units (SI) (Seitz et al. 2011; Pawlowicz et al. 2016). Seawater salinity is derived from electrical conductivity, temperature, and pressure in the current oceanographic practice [the Practical Salinity Scale of 1978 (PSS-78); IOC and SCOR and IAPSO 2010]. At present, it is possible to certify the electrical conductivity of SSW with traceability to the SI within an uncertainty of about 0.02% at the highest level (Seitz et al. 2019) and corresponding uncertainty of 0.008 in practical salinity. This level of uncertainty is too large to use in climate studies in the deep ocean (e.g., Levin et al. 2019; Purkey et al. 2019). Meanwhile, it is possible to measure salinity with traceability to the K_{15} value of SSW defined by the PSS-78 within a relative uncertainty of 0.002 in practical salinity (Guildline Instruments 2004), where the K_{15} is electrical conductivity ratio relative to a potassium chloride (KCl) solution ($32.4356 \text{ g kg}^{-1}$) at a temperature of 15°C [International Practical Temperature Scale of 1968 (IPTS-68)] and a pressure of one standard atmosphere. However, SSW is a metrological artifact and is subject to variations over time or between independent realizations (Seitz et al. 2011).

Several studies have reported systematic batch-to-batch differences for SSW (e.g., Aoyama et al. 2002; Kawano et al. 2006). For example, Kawano et al. (2006) reported batch-to-batch salinity offsets ranging from -0.9×10^{-3} to 2.5×10^{-3} on the practical salinity scale for SSW batches P91–P145. Kawano et al. (2005) concluded that the batch-to-batch offsets could result from inconsistency in the conductivity of the KCl standard solution defined by the PSS-78. Meanwhile, Bacon et al. (2007) reported recalibrated batch-to-batch offsets in reference to carefully prepared solutions of KCl and concluded that SSW batches P130–P144 had offsets effectively equal to zero within the expanded uncertainty (0.4×10^{-3} in practical salinity). Bacon et al. (2007) suggested that batch-to-batch offsets resulted from handling effects (motion and temperature changes during global shipping), especially for

older batches contained in soda-glass ampoules (produced before 2000), and that recent batches in borosilicate-glass bottles might hold the labeled conductivity ratio over longer periods, including transportation.

In this study, we expanded the batch-to-batch salinity offset table proposed by Kawano et al. (2006) for recent batches P145–P163 to check the magnitude of the offsets, which is expected to be small for recent batches (Bacon et al. 2007). We evaluated the expanded batch-to-batch correction table by applying it to time series of salinity data obtained in the deep ocean in recent decades. We also evaluated the SSW linearity pack (practical salinities of 10, 30 and 38) by applying the batch-to-batch correction.

2. Materials and methods

We used the P series (practical salinity of about 35) of SSW to estimate batch-to-batch offsets from batch P145 to P163. We also used the SSW linearity pack (Ocean Scientific International, Ltd.). In the linearity pack, SSW with practical salinities of 10 (10L series), 30 (30L series), and 38 (38H series) are available in addition to the P series for evaluating the linearity of salinometers. The linearity pack is produced from the same source seawater (northeastern Atlantic Ocean surface water) as that of the P series, with dilution by deionized water or concentration by evaporation.

The practical salinity of SSW was measured with a salinometer (Autosal model 8400B; Guildline Instruments, Ltd.). This salinometer has a practical salinity measurement range from 0.005 to 42 and a resolution of 0.0002 and is used to determine the label value of SSW as the de facto standard laboratory salinometer for high-quality salinity measurements. The salinometers were calibrated by using the P-series SSW, and the salinities of test samples were measured at 24°C , following the method of Kawano (2010).

The salinity measurements were conducted by the Japan Agency for Marine-Earth Science and Technology (JAMSTEC), except for the measurements to estimate the batch-to-batch offset for batch P153, which were conducted by the Japan Meteorological Agency (JMA).

We used the High-Accuracy Resistance Substituter (HARS) series of decade resistance substituter (model HARS-X-7-0.001-K from IET Laboratories, Inc.) to estimate linearity errors of the salinometers. The maximum resistance of this instrument is $11\,111.11 \, \Omega$ and zero resistance is less than $1 \text{ m}\Omega$ per decade, with a resolution of $1 \text{ m}\Omega$. The decade resistance substituter can be used with a four-wire Kelvin lead connection to replace the conductivity cell in the salinometer, as described in the user's manual (Guildline Instruments 2004). The double

FIG. 1. Schematic example of a batch-to-batch offset in the salinity of SSW. Normally five consecutive batches A–E are simultaneously measured to estimate the batch-to-batch offset of a target batch E. The measured salinities are calibrated against the batch-to-batch offset-corrected values by adjusting the mean value for the reference batches A–D except for the target batch E. The batch-to-batch offset for the target batch is estimated from the difference between the thus calibrated value and the label value.

conductivity ratio $2K$ can be determined by the decade resistance substituter as

$$2K = 2R_{2.0}/R, \quad (1)$$

where $R_{2.0}$ is the resistance of the decade resistance substituter at a salinometer reading of 2.0 and R is the resistance of the decade resistance substituter for obtaining a chosen $2K$ value. For example, if it is desired to obtain 1.0 as the $2K$ value, the R should be set to the value of $2R_{2.0}$.

3. Evaluation of P-series SSW

We evaluated the certified double conductivity ratios of the P-series SSW (practical salinity of about 35) using measurements of double conductivity ratios by the salinometer. Since we can only evaluate the batch-to-batch offset of a target batch relative to a known estimated “true value,” we referred to the batch-to-batch offset-corrected salinities proposed by Kawano et al. (2006) with reference to the average of the batch-to-batch offsets for batches P130–P145, taking the comparability into consideration.

Several consecutive batches of SSW, including a target batch for which the batch-to-batch offset was to be determined, were measured simultaneously every time

that a new batch of SSW was produced. Figure 1 is a schematic of the method for estimating the batch-to-batch offset. The manufacturer claims a 3-yr shelf life for SSW based on their stability tests (Culkin and Ridout 1998). However, because of the uncertainty of measurements, it is desirable to use as many batches as possible for reference to estimate the batch-to-batch offset of the target batch. In principle, therefore, at the time of measurement we used five consecutive batches, including the target batch as the most recent (see appendix A for more details), because SSW is stable for 5 years after calibration (Bacon et al. 2007) (see also Fig. A1).

The expanded batch-to-batch offsets in practical salinity relative to the new reference proposed by Kawano et al. (2006) up to P163 are listed in Table 1 and shown in Fig. 2. The batch-to-batch offset for P145 was reevaluated because the difference between the value proposed by Kawano et al. (2006) and the value in this study was quite large (1.1×10^{-3} in practical salinity) and no values consistent with that proposed by Kawano et al. (2006) have been obtained since those measurements (see Table A1 for more details). The average of the expanded batch-to-batch offsets (from P145 to P163) was close to zero (-0.19×10^{-3} in practical salinity), but sometimes the magnitude of the offset was larger than the expanded uncertainty (0.4×10^{-3} in practical salinity; Bacon et al. 2007); for example, the estimated offset for P146 was 3 times the expanded uncertainty.

Standardization of the salinometer involves changing the span of the slope of the salinometer by adjusting it to the labeled conductivity ratio of the SSW. Time drift of the salinometer is also a change in the span of the

FIG. 2. Batch-to-batch offsets in practical salinity for IAPSO Standard Seawater. Triangles are from Kawano et al. (2006), circles are from this study, and squares are from Bacon et al. (2007). Dashed lines show the expanded uncertainty of the label salinity (Bacon et al. 2007).

TABLE 1. Batch-to-batch offsets in practical salinity and correction factors for IAPSO Standard Seawater. The correction factors for the previous batches (P91–P144) are also available online (<http://www.jamstec.go.jp/datadoi/doi/10.17596/0001983.html>), and the online database will be expanded for the most recent batches.

Batch No.	Date of preparation	K_{15}	Salinity (PSS-78)	Offset ($\times 10^{-3}$)	Correction factor
P145	15 Jul 2004	0.999 81	34.9926	−1.0	0.999 971 4
P146	12 May 2005	0.999 79	34.9918	−1.5	0.999 957 1
P147	06 Jun 2006	0.999 82	34.9930	−0.6	0.999 982 9
P148	01 Oct 2006	0.999 82	34.9930	0.0	1.000 000 0
P149	5 Oct 2007	0.999 84	34.9937	0.7	1.000 020 0
P150	22 May 2008	0.999 78	34.9914	0.7	1.000 020 0
P151	20 May 2009	0.999 97	34.9988	−0.5	0.999 985 7
P152	5 May 2010	0.999 81	34.9926	−0.1	0.999 997 1
P153	8 Mar 2011	0.999 79	34.9918	0.4	1.000 011 4
P154	20 Oct 2011	0.999 90	34.9961	0.5	1.000 014 3
P155	19 Sep 2012	0.999 81	34.9926	0.1	1.000 002 9
P156	23 Jul 2013	0.999 84	34.9937	0.4	1.000 011 4
P157	15 May 2014	0.999 85	34.9941	−0.8	0.999 977 1
P158	25 Mar 2015	0.999 70	34.9883	−0.2	0.999 994 3
P159	15 Dec 2015	0.999 88	34.9953	−0.4	0.999 988 6
P160	20 Jul 2016	0.999 83	34.9933	0.0	1.000 000 0
P161	3 May 2017	0.99 987	34.9949	−0.2	0.999 994 3
P162	16 Apr 2018	0.999 83	34.9933	−0.5	0.999 985 7
P163	10 Apr 2019	0.999 85	34.9941	−0.6	0.999 982 9

slope (see [appendix B](#)). Strictly speaking, the batch-to-batch offset correction does not reflect this nature of standardization. Therefore, there could be an error in case of applying a large batch-to-batch offset. Nonetheless, the offset correction is usually adequate for real seawater samples, as demonstrated by previous studies (e.g., [Kawano et al. 2006](#)), because the salinity range for 99% of the world's ocean waters (33–37 g kg^{−1}; [Millero 2006](#)) is close to the salinity of SSW (about 35 g kg^{−1}). However, for salinities much lower or higher than 35 g kg^{−1}, the offset correction introduces an artificial error.

If the batch-to-batch offset is 0.0015 in practical salinity (maximum in [Table 1](#)), the artificial error becomes detectable (greater than the resolution of the salinometer) for practical salinity higher than 40 or lower than 30. Considering the measurement range of the salinometer (0.005–42 in practical salinity), this becomes a significant issue for measurements in low salinity regions affected by river runoff or meltwater [e.g., surface water of the Arctic Ocean ([Millero et al. 2010](#)) and Baltic Sea ([Feistel et al. 2010](#))]. It is therefore recommended that the correction factors ([Table 1](#)) be used instead of using the offsets to correct the batch-to-batch differences of SSW by multiplying the salinity by the correction factor, as there is a linear relationship between the conductivity ratio and salinity.

4. Evaluation of the batch-to-batch correction table

We evaluated the expanded batch-to-batch correction factors ([Table 1](#)) by applying them to the

conductivity–temperature–depth (CTD) salinity data collected in the northwestern North Pacific Ocean. Bottom water in the northern North Pacific originates from the Circumpolar Deep Water that flows northward from the Southern Ocean, and its water properties [such as the temperature–salinity (T – S) relationship] is expected to be relatively uniform for a long time as bottom water is not formed in the North Pacific.

We collected full-depth CTD data obtained from R/V *Mirai* at time series station K2 [47°N, 160°E; water depth 5215 m; see [Wakita et al. \(2017\)](#) for more detail]. The CTD data are available online (<http://www.godac.jamstec.go.jp/k2/> and <https://ebcrpa.jamstec.go.jp/k2s1/en/>). Station K2 is one of the CTD stations along WOCE Hydrographic Program (WHP) line P01; high-accuracy hydrographic observations were conducted along line P01 in 1985 (<https://cchdo.ucsd.edu/cruise/31TTTPS47>), 1999 ([Uchida et al. 2002](#)), 2007 ([Kawano et al. 2009](#)) and 2014 ([Uchida and Doi 2017](#)). Station K2 is also one of the CTD stations of the repeat hydrographic section maintained by the JMA. Full-depth CTD observations have been conducted at station K2 by R/Vs *Ryofu-maru* and *Keifu-maru* once per year since 2011, except for 2012; the CTD data are available online (https://www.data.jma.go.jp/gmd/kaiyou/db/vessel_obs/data-report/html/ship/ship_e.php). Station K2 bottom water is therefore a good choice for applying the batch-to-batch corrections.

[Figure 3](#) shows the T – S relationship for the bottom water at station K2. Variation in the T – S relationship was reduced by applying the batch-to-batch correction

FIG. 3. Temperature–salinity relationship for the bottom water in the northwestern North Pacific Ocean (47°N, 160°E) derived from shipboard CTD data (37 profiles) obtained from 1985 to 2019 (31 cruises) for (a) original salinity data, and (b) the salinity data after applying the batch-to-batch correction. Reference salinity and potential temperature were calculated from the Thermodynamic Equation of Seawater–2010 (TEOS-10).

to the CTD salinity data (Fig. 3b), especially for the WHP data in 1985, as also shown by Kawano et al. (2006). The T – S relationship is almost linear for the range plotted in Fig. 3; we therefore examined the temporal variation of the T – S relationship by extracting salinity at a potential temperature of 1.09°C as estimated from the regression line between 1.08° and 1.10°C for each CTD profile (Fig. 4). The original salinity data showed a decadal time-scale undulation [high (34.8544 g kg^{−1}) around 2006, low (34.8514 g kg^{−1}) around 2014, and relatively high (34.8526 g kg^{−1}) around 2019]. However, this undulation disappeared after applying the batch-to-batch correction factors to the salinity data, and a linear trend of slight freshening ($-0.6 \pm 0.1 \times 10^{-3}$ g kg^{−1} per decade^{−1}) was detected. This slight linear trend is more likely than short-term large changes in the water-mass properties of the bottom water and might be related to a reduction of the formation rate of Antarctic Bottom Water as inferred in the South Pacific Ocean (Purkey et al. 2019). This result suggests that the batch-to-batch difference correction is extremely important for detecting salinity changes in the deep ocean for climate studies.

5. Evaluation of the SSW linearity pack

Unlike the P-series salinity standards, the label salinities of the linearity pack (series 10L, 30L, and 38H) were certified by using a salinometer (Autosal model 8400B; Guildline Instruments, Ltd.) calibrated by using the P-series SSW. Therefore, for precise evaluation of

FIG. 4. Time series of reference salinity at potential temperature of 1.09°C (average pressure of 4688 dbar) extracted from the CTD data shown in Fig. 3. Open circles represent original salinity data, and closed circles are salinity data after applying the batch-to-batch correction. The solid and dashed lines are the regression line and the standard deviation from the regression line for the batch-to-batch-corrected salinity data. A decadal trend of slight freshening ($-0.6 \pm 0.1 \times 10^{-3}$ g kg^{−1} decade^{−1}) was observed, and the standard deviation from the regression line is 0.7×10^{-3} and 0.3×10^{-3} g kg^{−1} for the original salinity data and the corrected salinity data, respectively. There were no CTD data calibrated with batches 134–138, 140, 143, 147, 149, 150, or 158.

the linearity pack, the batch-to-batch offset correction should be applied to the label salinity in addition to the batch-to-batch correction for the measured salinity of the linearity pack.

We measured several batches of the linearity pack. The label salinity was calibrated by using P-series SSW (P150 for 38H10, P149 for 30L14 and 10L11, and P158 for 10L15; R. Williams, Ocean Scientific International, Ltd., 2019, personal communication). The batch-to-batch correction factors were applied to the label salinity and the measured salinity (Table 2). The measured salinity agreed well with the label salinity (within ± 0.0001 in practical salinity) for batches 30L14 and 38H10. However, for batches 10L11 and 10L15, the difference between the label value and measured value was relatively large (0.0007–0.0011 in practical salinity). We then estimated the linearity errors of the salinometers by using decade resistance substituters and compared these results with those of the linearity pack measurements.

The double conductivity ratio $2K$ was determined at each step of the suppression dial, which changes the number of the resistors in series (23 steps for the full range of double conductivity ratios from 0 to 2.2) by adjusting the resistance R of the decade resistance substituter from Eq. (1) and then measuring the ratio with the salinometer. Differences in salinity calculated from the measured $2K$ values and those determined from the decade resistance substituters were plotted for six

TABLE 2. Practical salinity measurements of the SSW linearity pack. The number of bottles measured and the batch number of the SSW used for calibration of the salinometer are shown in parentheses following the measured salinity.

Batch No.	Date of calibration	Label salinity (PSS-78)	Date of measurement	Measured salinity (PSS-78)
38H10	1 Oct 2008	37.9975	20 Mar 2009	37.9974 ($n = 3$; P150) ^a
30L14	29 Sep 2008	30.0030	20 Mar 2009	30.0030 ($n = 3$; P150) ^a
10L11	23 Jul 2008	9.9985	20 Mar 2009	9.9992 ($n = 3$; P150) ^a
10L15	17 Jun 2015	9.9958	25 Dec 2015	9.9967 ($n = 2$; P157) ^b
10L15	17 Jun 2015	9.9958	23 Jan 2017	9.9967 ($n = 2$; P159) ^b
10L15	17 Jun 2015	9.9958	05 Apr 2017	9.9969 ($n = 2$; P159) ^c

^a Measured using Autosol serial No. 62827.

^b Autosol serial No. 62556.

^c Autosol serial No. 71758.

salinometers (Fig. 5). For the three salinometers used in the linearity pack measurements (serial numbers 62827, 62556, and 71758), the salinity errors estimated from the decade resistance substituters were consistent with the salinity differences seen in the linearity pack measurements. This suggests that most of the relatively large salinity differences (0.0007–0.0011 in practical salinity) for the 10L series can be explained by the linearity error of the salinometers, excluding a contribution from the conductivity cell. Any linearity error in the salinometer used by the manufacturer for the calibration of the linearity pack could also contribute to the rest (about 0.0005 in practical salinity) of the relatively large salinity differences. The repeatability of

the decade resistance substituter measurements is discussed in appendix C.

6. Discussion

Kawano et al. (2006) reported the batch-to-batch offsets of IAPSO SSW up to batch P145 by conducting intercomparisons of IAPSO SSW measurements, as in this study: they concluded that the standard deviation of batch-to-batch differences of recent (at that time) batches (P130 to P145) had been reduced (0.3×10^{-3} in practical salinity) and was comparable to the resolution of the salinometer (0.2×10^{-3} in practical salinity). Bacon et al. (2007) also reported batch-to-batch

FIG. 5. Linearity errors in practical salinity estimated from measurements of the SSW linearity pack listed in Table 2 (closed circles, closed triangles, and a closed inverted triangle) and measurements of the decade resistance substituters (open circles, open triangles, open inverted triangles, and letters A, B, and C), by replacing the conductivity cell with the decade resistance substituter. The linearity errors for three salinometers estimated from the linearity pack were reasonably consistent with the errors estimated from the decade resistance substituters. Two closed triangles at salinity of 10 overlap.

differences of IAPSO SSW by recalibrating in reference to carefully prepared solutions of KCl for recent (at that time) batches (P130–P144), and batch-to-batch offsets estimated from newly calibrated data obtained within the shelf life (3 years from the original calibration date) are shown in Fig. 2. Bacon et al. (2007) found no significant change in label salinity outside the expanded uncertainty (0.4×10^{-3} in practical salinity). The standard deviation (0.3×10^{-3} in practical salinity) of batch-to-batch offsets from Bacon et al. (2007) was also comparable to the resolution of the salinometer.

Six batches (P138, P139, P141, P142, P143, and P144) overlapping between Kawano et al. (2006) and this study were measured totally 16 times to check consistency between the two studies, although ages of these batches were older than 5 years at the time of measurements [identifier (ID) “N” in Table A1]. Mean with the standard error of the differences from the batch-to-batch offset-corrected values for the above 16 measurements was 0.0003 ± 0.0001 in practical salinity. The mean value was not different from the resolution of the salinometer (0.0002 in practical salinity), although the mean value might include the effect of evaporation of water due to long-term storage. These results suggest that Kawano et al. (2006) and this study are consistent with each other, except for P145.

In Kawano et al. (2006), the batch P145 was measured at JAMSTEC and the Woods Hole Oceanographic Institution in 2005, and these two results were consistent with each other. In this study, the batch P145 was measured at JAMSTEC, in 2006, 2007, 2009, and 2010 and at JMA in 2011, and these five results were consistent with each other. Although the reason of the inconsistency for the batch P145 between Kawano et al. (2006) and this study is unknown, the estimated offset in this study is reasonable judging from the tendency of the freshening in the deep North Pacific (Fig. 4).

As suggested in these previous studies, the batch-to-batch differences are small for recent batches, but the difference sometimes deviates beyond the expanded uncertainty (e.g., -0.0015 in practical salinity for batch P146). The standard deviation of the batch-to-batch differences proposed by this study (P145–P163) was 0.0006 in practical salinity. Therefore, uncertainty of salinity changes in the recent decade is statistically expected to be reduced by 0.0006 in practical salinity by applying the batch-to-batch correction. In fact, the standard deviation from the decadal trend of the deep North Pacific freshening (Fig. 4) was reduced from 0.0007 to 0.0003 g kg^{-1} by applying the batch-to-batch correction. Magnitude of the reduction was estimated to be $0.0006 \text{ g kg}^{-1} [\sqrt{(0.0007^2 - 0.0003^2)}]$ and agreed

well with the standard deviation of the batch-to-batch differences.

Howell et al. (2010) presented large shift (about $+0.0013$ in practical salinity) of measured salinity values for their in-house standard seawater when they began using SSW P151 instead of using P150 for the calibration of their salinometer. This large shift can be completely explained by the batch-to-batch offsets proposed by this study ($+0.0007$ and -0.0005 in practical salinity for P150 and P151, respectively).

The batch-to-batch correction was also successfully applied to recent international hydrographic data to detect freshening of bottom water in the South Pacific Ocean (Purkey et al. 2019), although additional ad hoc offsets were sometimes required for older data from the 1990s to improve internal consistency of the salinity dataset (Purkey et al. 2019). The standard deviation of the batch-to-batch differences proposed by Kawano et al. (2006) and this study since 1980 (P91–P163) was 0.0009 in practical salinity. Therefore, uncertainty of salinity difference due to the batch-to-batch differences between two hydrographic sections a few decades apart can be estimated to be 0.0013 in practical salinity $[\sqrt{(0.0009^2 + 0.0009^2)}]$. Magnitude of the uncertainty due to the batch-to-batch differences is comparable to the basin mean deep freshening (0.0013 in practical salinity per decade) observed in the South Pacific Ocean (Purkey et al. 2019). These results suggest that the batch-to-batch correction is effective for deep-ocean salinity data to evaluate and to monitor deep ocean salinity changes.

Older SSWs (batches before P140) were sealed in soda-glass ampoules. The soda glass of the ampoules had a lower quality than the borosilicate glass of the bottles used for more recent SSWs (batches after P140), and the ampoules had a larger air space than the bottles. The larger air space allows more “sloshing” inside the ampoules with any motion (Bacon et al. 2007). Bacon et al. (2007) hypothesized that motion and temperature changes are important agents causing batch-to-batch differences of SSW. If this is true, then a reference seawater more robust and stable than SSW is necessary to allow SSW users worldwide to estimate batch-to-batch differences of the SSWs used in their laboratories and on ships.

Such reference seawater must have long-term stability at least in terms of practical salinity, especially against motion and temperature changes. The Chinese Primary Standard Seawater for practical salinity measurement is distributed in borosilicate glass bottles with air space in the bottle (Li et al. 2016), similar to IAPSO SSW, and therefore will have the same problems. On the other hand, the Multiparametric Standard Seawater (MSSW) currently under development jointly by KANSO Co., Ltd., Osaka, Japan, and JAMSTEC might be a candidate for such reference seawater.

FIG. 6. Stability in practical salinity with storage time (yr) for the Multiparametric Standard Seawater (lot Pre16, produced on 6 Sep 2012). Open circles indicate original salinity data, and closed circles indicate salinity data after applying the batch-to-batch correction for IAPSO SSW. From two to five bottles of Pre16 were measured at each measurement, and the measured salinity data were averaged to evaluate stability in practical salinity. The solid and dashed lines indicate mean and $\pm$ standard deviation (SD) of the salinity data after applying the batch-to-batch correction.

MSSW uses 500-ml aluminum beverage bottles (New Bottle Can; Daiwa Can Company) with highly functional plastic inner caps and is produced by a method similar to that used for the Reference Material for Nutrients in Seawater (RMNS) (KANSO Co., Ltd.), with no air space in the bottle. MSSW is intended for use as a reference for practical salinity, density, nutrients, dissolved inorganic carbon, total alkalinity, dissolved organic carbon, pH and dissolved oxygen because of its high-performance gas and water-vapor barrier. Source seawater for MSSW was collected from 400-m depth in Suruga Bay, south of Shizuoka, Japan. Typical values of the properties are 34.352 (practical salinity), $1024.278 \text{ kg m}^{-3}$ (density at 20°C), $44 \mu\text{mol kg}^{-1}$ (silicate), $12 \mu\text{mol kg}^{-1}$ (nitrate), $2222 \mu\text{mol kg}^{-1}$ (dissolved inorganic carbon), $2303 \mu\text{mol kg}^{-1}$ (total alkalinity), $90 \mu\text{mol kg}^{-1}$ (dissolved organic carbon), 7.6 (pH at 25°C) and $210 \mu\text{mol kg}^{-1}$ (dissolved oxygen). The change in practical salinity after an accelerated test (three bottles were exposed to a temperature of 60°C for 10 days) was 0.0001 ± 0.0002 (lot Pre16), relative to -0.0002 ± 0.0002 for IAPSO SSW (batch P153), and there was little change in practical salinity during storage for seven years at room temperature (about 24°C) (Fig. 6). The standard deviation of the repeated practical salinity measurements of MSSW over seven years was reduced from 0.36×10^{-3} to 0.26×10^{-3} by applying the batch-to-batch correction of IAPSO SSW, and was close to the resolution of the salinometer (0.2×10^{-3} in practical salinity).

Previous studies have reported linearity errors in salinometers greater than the manufacturer's specifications

[± 0.003 in practical salinity for Autosol model 8400B (Li et al. 2018) and ± 0.005 in practical salinity for Portasal model 8410A (Le Menn 2011)]. Li et al. (2018) recommended checking the linearity error of the salinometer by using not only the SSW linearity pack [practical salinities of 10, 20, 30, 35, and 38 (20 is not currently available)] but also by in-house weight dilution of seawater samples for subranges of the linearity pack (practical salinities of 5, 15, 25, 33, and 36), and to remove the linear trend of the error for each selected salinity range. In this study, however, we did not observe linearity errors above the manufacturer's specifications (± 0.002 in practical salinity; Guildline Instruments, Ltd.) in six Autosol 8400B salinometers (Fig. 5), and the linearity error distributions did not follow any clear pattern and rarely spiked (around 1 in practical salinity for salinometer serial number 62827). Therefore, to correct the linearity error of a salinometer, it might be suitable to use the detailed distribution estimated from the decade resistance substituter rather than using linear trends estimated from the linearity pack measurements.

Although the batch-to-batch correction for IAPSO SSW is practically efficient for establishing comparability for salinity measurements in oceanography and climatology, as shown in Figs. 3 and 4, the lack of traceability to the SI with sufficiently small uncertainty in salinity measurements (at a level of $10^{-3} \text{ g kg}^{-1}$) is a fundamental problem (Seitz et al. 2011, 2019). Therefore, Pawlowicz et al. (2016) recommended measuring the density of IAPSO SSW to establish traceability of absolute salinity to the SI with an uncertainty of $5 \times 10^{-3} \text{ g kg}^{-1}$. However, the resolution of the density (or absolute salinity) measurement for the de facto standard oscillation-type density meter ($1 \times 10^{-3} \text{ kg m}^{-3}$; DMA 5000M, Anton-Paar GmbH) is an order of magnitude larger than that of the conductivity salinometer ($0.15 \times 10^{-3} \text{ kg m}^{-3}$), and the density meter may have a linearity error ($\sim 6 \times 10^{-3} \text{ kg m}^{-3}$) in the seawater density measurements (Uchida et al. 2011). The interference method, on the other hand, is one of the most sensitive methods for measuring the refractive index (or density) of seawater. There is now an ultrahigh-resolution ($0.1 \times 10^{-3} \text{ kg m}^{-3}$) density sensor based on measuring the refractive index by the interference method (Uchida et al. 2019). This density sensor will contribute substantially toward establishing the traceability of salinity measurements, and it will be suitably calibrated by using MSSW, because density-related parameters (practical salinity, nutrient concentrations, and carbonate system parameters; Pawlowicz et al. 2011) and thus density of MSSW are expected to be more stable than SSW whose density increases with time by dissolution of silicate from the glass bottles (Uchida et al. 2011).

7. Conclusions

We expanded the batch-to-batch salinity offset table of the IAPSO SSW proposed by Kawano et al. (2006) for recent batches P145–P163 by intercomparison measurements using salinometers (Autosal model 8400B). Several consecutive batches (within five years from production), including the target batch for which the batch-to-batch offset was to be determined, were measured simultaneously every time that a new batch of SSW was produced. Also, six batches overlapping between Kawano et al. (2006) and this study were measured, although ages of these batches were older than five years at the time of measurements. We confirmed that the batch-to-batch offset tables proposed by Kawano et al. (2006) and this study are consistent with each other, except for P145. As suggested in the previous studies, the batch-to-batch differences are small for recent batches (the standard deviation for P145–P163 was 0.0006 in practical salinity), but the difference sometimes deviates beyond the expanded uncertainty (e.g., -0.0015 in practical salinity for P146).

We recommend using the correction factors instead of the offsets to correct the batch-to-batch differences, especially for salinity data much lower or higher than 35 g kg^{-1} , because standardization of the salinometer involves changing the span of the slope of the salinometer. Time drift of the salinometer is also a change of the span of the slope. The offset correction introduces an artificial error for salinities much lower or higher than 35 g kg^{-1} . If the batch-to-batch offset is 0.0015 in practical salinity, the artificial error become detectable for practical salinity higher than 40 or lower than 30.

We evaluated the expanded batch-to-batch correction factors by applying them to time series CTD salinity data collected in the northwestern North Pacific Ocean in recent decades. We examined the temporal variation of the T – S relationship by extracting salinity at a potential temperature of 1.09°C . Although the original salinity data showed a decadal time-scale undulation, the undulation disappeared after applying the batch-to-batch correction factors to the salinity data, and a linear trend of slight freshening ($-0.6 \pm 0.1 \times 10^{-3} \text{ g kg}^{-1} \text{ decade}^{-1}$) was detected. The slight freshening might be related to a reduction of the formation rate of Antarctic Bottom Water. We suggest that the batch-to-batch correction is extremely important for detecting salinity changes in the deep ocean for climate studies.

We also evaluated the SSW linearity pack (practical salinities of 10, 30, and 38) by applying the batch-to-batch correction factors. Linearity errors of the salinometers estimated from decade resistance substituters were consistent with the results of the linearity pack measurements. Although the linearity errors estimated from the decade

resistance substituters were within the manufacturer's specification (± 0.002 in practical salinity) in six Autosal 8400B salinometers, the linearity error distributions did not allow any clear pattern and rarely spiked. Therefore, to correct the linearity error of a salinometer, it might be suitable to use the detailed distribution estimated from the decade resistance substituter rather than using linear trends estimated from the linearity pack measurements.

Although the reasons for the batch-to-batch differences beyond the expanded uncertainty are unknown, motion and temperature changes might be important agents causing batch-to-batch differences of SSW, then a reference seawater more robust and stable than SSW is necessary to allow SSW users worldwide to estimate batch-to-batch differences of the SSWs used in their laboratories and on ships. Moreover, the lack of traceability to the SI with sufficiently small uncertainty in salinity measurements is a fundamental problem and measuring the density of SSW is recommended to establish traceability of absolute salinity to the SI. MSSW currently under development might be a candidate for such reference seawater, because MSSW is expected to be more stable than SSW not only in practical salinity but also in absolute salinity. The ultrahigh-resolution density sensor based on measuring refractive index by the interference method will contribute substantially toward establishing the traceability of salinity measurements to the SI, and it will be suitably calibrated by using MSSW.

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APPENDIX A

Details of Batch-to-Batch Offset Measurements

Details of measurements for determining the batch-to-batch offsets shown in Table 1 are presented in Table A1 and

TABLE A1. Results of measurements to determine the batch-to-batch offsets shown in Table 1. In the “identification label” (ID) column, D indicates batches whose offsets were determined, R indicates batches used as a reference, and N indicates batches that were not used for determination of the offsets. The number of bottles measured (Num), and the difference in practical salinity from the label value for bottles with ID D or from the batch-to-batch offset-corrected values (see Table 1) for R and N bottles are also shown.

ID	Batch No.	Salinity $\pm$ SD (PSS-78)	Num	Calibrated salinity (PSS-78)	Diff ($\times 10^{-3}$)	Correction factor
Determination of P145, P146, and P147 (date of measurements: 6 Jul 2006)						
N	P138	34.9989 $\pm$ 0.0004	5	34.9984	0.8	
N	P141	34.9980 $\pm$ 0.0002	5	34.9975	0.5	
R	P142	34.9974 $\pm$ 0.0003	5	34.9969	0.2	
R	P144	34.9948 $\pm$ 0.0004	5	34.9943	−0.1	
D	P145	34.9921 $\pm$ 0.0001	5	34.9916	−1.0	0.999 971 4
D	P146	34.9908 $\pm$ 0.0002	5	34.9903	−1.5	0.999 957 1
D	P147	34.9929 $\pm$ 0.0002	7	34.9924	−0.6	0.999 982 9
Determination of P148 (date of measurements: 30 May 2007)						
N	P138	34.9989 $\pm$ 0.0004	5	34.9989	1.3	
N	P139	34.9978 $\pm$ 0.0002	5	34.9978	0.1	
N	P141	34.9973 $\pm$ 0.0003	5	34.9973	0.3	
N	P142	34.9974 $\pm$ 0.0001	5	34.9974	0.7	
R	P144	34.9943 $\pm$ 0.0004	7	34.9943	−0.1	
R	P145	34.9915 $\pm$ 0.0005	7	34.9915	−0.1	
R	P146	34.9905 $\pm$ 0.0001	7	34.9905	0.2	
R	P147	34.9923 $\pm$ 0.0002	9	34.9923	−0.1	
D	P148	34.9930 $\pm$ 0.0001	9	34.9930	0.0	1.000 000 0
Determination of P149 and P150 (date of measurements: 19 Jan 2009)						
N	P144	34.9952 $\pm$ 0.0001	3	34.9945	0.1	
N	P145	34.9924 $\pm$ 0.0005	3	34.9917	0.1	
R	P146	34.9911 $\pm$ 0.0002	3	34.9904	0.1	
R	P147	34.9928 $\pm$ 0.0002	4	34.9921	−0.3	
R	P148	34.9938 $\pm$ 0.0001	7	34.9931	0.1	
D	P149	34.9951 $\pm$ 0.0002	9	34.9944	0.7	1.000 020 0
D	P150	34.9928 $\pm$ 0.0002	9	34.9921	0.7	1.000 020 0
Determination of P151 and P152 (date of measurements: 25 Aug 2010)						
N	P144	34.9940 $\pm$ 0.0001	5	34.9939	−0.5	
N	P145	34.9913 $\pm$ 0.0002	3	34.9912	−0.4	
N	P146	34.9898 $\pm$ 0.0006	3	34.9897	−0.6	
N	P147	34.9914 $\pm$ 0.0003	5	34.9913	−1.1	
R	P148	34.9932 $\pm$ 0.0003	4	34.9931	0.1	
R	P149	34.9945 $\pm$ 0.0002	4	34.9944	0.0	
R	P150	34.9920 $\pm$ 0.0002	5	34.9919	−0.2	
D	P151	34.9984 $\pm$ 0.0002	4	34.9983	−0.5	0.999 985 7
D	P152	34.9926 $\pm$ 0.0002	6	34.9925	−0.1	0.999 997 1
Determination of P153 (date of measurements: 17 Aug 2011)						
N	P141	34.9972 $\pm$ 0.0004	5	34.9976	0.6	
N	P143	34.9961 $\pm$ 0.0002	5	34.9965	1.0	
N	P144	34.9942 $\pm$ 0.0003	4	34.9946	0.2	
N	P145	34.9911 $\pm$ 0.0002	5	34.9915	−0.1	
N	P146	34.9897 $\pm$ 0.0001	5	34.9901	−0.2	
N	P147	34.9914 $\pm$ 0.0004	5	34.9918	−0.6	
N	P148	34.9928 $\pm$ 0.0003	5	34.9932	0.2	
R	P149	34.9942 $\pm$ 0.0002	5	34.9946	0.2	
R	P150	34.9917 $\pm$ 0.0002	5	34.9921	0.0	
R	P151	34.9978 $\pm$ 0.0002	5	34.9982	−0.1	
R	P152	34.9922 $\pm$ 0.0002	6	34.9926	0.1	
D	P153	34.9918 $\pm$ 0.0003	20	34.9922	0.4	1.000 011 4
Determination of P154 (date of measurements: 16 Apr 2012)						
R	P151	34.9980 $\pm$ 0.0003	5	34.9983	0.0	
R	P152	34.9922 $\pm$ 0.0002	5	34.9925	0.0	
R	P153	34.9918 $\pm$ 0.0003	11	34.9921	−0.1	
D	P154	34.9963 $\pm$ 0.0001	5	34.9966	0.5	1.000 014 3

TABLE A1. (Continued)

ID	Batch No.	Salinity $\pm$ SD (PSS-78)	Num	Calibrated salinity (PSS-78)	Diff ($\times 10^{-3}$)	Correction factor
Determination of P155 (date of measurements: 15 May 2013)						
R	P151	34.9981 $\pm$ 0.0001	5	34.9984	0.1	1.000 002 9
R	P152	34.9922 $\pm$ 0.0002	5	34.9925	0.0	
R	P153	34.9919 $\pm$ 0.0001	5	34.9922	0.0	
R	P154	34.9964 $\pm$ 0.0002	5	34.9967	0.1	
D	P155	34.9924 $\pm$ 0.0002	9	34.9927	0.1	
Determination of P156 (date of measurements: 6 Jun 2014)						
R	P152	34.9925 $\pm$ 0.0002	5	34.9929	0.4	1.000 011 4
R	P153	34.9917 $\pm$ 0.0001	5	34.9921	−0.1	
R	P154	34.9959 $\pm$ 0.0002	5	34.9963	−0.3	
R	P155	34.9923 $\pm$ 0.0001	5	34.9927	0.0	
D	P156	34.9937 $\pm$ 0.0002	8	34.9941	0.4	
Determination of P157 (date of measurements: 19 Nov 2014)						
N	P152	34.9922 $\pm$ 0.0002	5	34.9924	−0.1	0.999 977 1
R	P153	34.9919 $\pm$ 0.0003	5	34.9921	−0.1	
R	P154	34.9963 $\pm$ 0.0003	5	34.9965	−0.1	
R	P155	34.9928 $\pm$ 0.0003	5	34.9930	0.3	
R	P156	34.9938 $\pm$ 0.0003	5	34.9940	−0.1	
D	P157	34.9931 $\pm$ 0.0003	5	34.9933	−0.8	
Determination of P158 (date of measurements: 27 Dec 2015)						
N	P153	34.9932 $\pm$ 0.0004	5	34.9923	0.1	0.999 994 3
R	P154	34.9971 $\pm$ 0.0001	5	34.9962	−0.4	
R	P155	34.9940 $\pm$ 0.0002	5	34.9931	0.4	
R	P156	34.9950 $\pm$ 0.0001	5	34.9941	0.0	
R	P157	34.9941 $\pm$ 0.0003	5	34.9932	−0.1	
D	P158	34.9890 $\pm$ 0.0004	5	34.9881	−0.2	
Determination of P159 (date of measurements: 14 Feb 2017)						
N	P141	34.9977 $\pm$ 0.0001	2	34.9971	0.1	0.999 988 6
N	P144	34.9945 $\pm$ 0.0006	2	34.9939	−0.5	
N	P148	34.9934 $\pm$ 0.0004	2	34.9928	−0.2	
R	P155	34.9934 $\pm$ 0.0002	5	34.9928	0.1	
R	P156	34.9946 $\pm$ 0.0002	5	34.9940	−0.1	
R	P157	34.9939 $\pm$ 0.0001	5	34.9933	0.0	
R	P158	34.9885 $\pm$ 0.0002	5	34.9879	−0.2	
D	P159	34.9955 $\pm$ 0.0003	5	34.9949	−0.4	
Determination of P160 (date of measurements: 14 Jul 2017)						
R	P156	34.9938 $\pm$ 0.0003	5	34.9941	0.0	1.000 000 0
R	P157	34.9931 $\pm$ 0.0002	5	34.9934	0.1	
R	P158	34.9876 $\pm$ 0.0001	5	34.9879	−0.2	
R	P159	34.9949 $\pm$ 0.0001	5	34.9952	0.3	
D	P160	34.9930 $\pm$ 0.0003	5	34.9933	0.0	
Determination of P161 (date of measurements: 23 Jul 2018)						
R	P157	34.9935 $\pm$ 0.0003	5	34.9934	0.1	0.999 994 3
R	P158	34.9882 $\pm$ 0.0002	5	34.9881	0.0	
R	P159	34.9950 $\pm$ 0.0003	5	34.9949	0.0	
R	P160	34.9933 $\pm$ 0.0002	5	34.9932	−0.1	
D	P161	34.9948 $\pm$ 0.0002	4	34.9947	−0.2	
Determination of P162 (date of measurements: 6 May 2019)						
R	P158	34.9887 $\pm$ 0.0001	5	34.9882	0.1	0.999 985 7
R	P159	34.9955 $\pm$ 0.0001	5	34.9950	0.1	
R	P160	34.9936 $\pm$ 0.0001	4	34.9931	−0.2	
R	P161	34.9953 $\pm$ 0.0001	5	34.9948	0.1	
D	P162	34.9933 $\pm$ 0.0002	5	34.9928	−0.5	

TABLE A1. (Continued)

ID	Batch No.	Salinity $\pm$ SD (PSS-78)	Num	Calibrated salinity (PSS-78)	Diff ($\times 10^{-3}$)	Correction factor
Determination of P163 (date of measurements: 25 Jan 2020)						
R	P159	34.9954 ± 0.0002	5	34.9950	0.1	
R	P160	34.9935 ± 0.0002	5	34.9931	-0.2	
R	P161	34.9951 ± 0.0002	5	34.9947	0.0	
R	P162	34.9933 ± 0.0003	5	34.9929	0.1	
D	P163	34.9939 ± 0.0001	5	34.9935	-0.6	0.999 982 9

are also available online (<http://www.jamstec.go.jp/datadoi/doi/10.17596/0001983.html>). The correction factor was calculated for ID “D” bottles. Relatively older batches of standard seawater were sometimes simultaneously measured in addition to several consecutive batches to determine the batch-to-batch offset (Fig. 1). Differences in practical salinity from the batch-to-batch corrected values are shown in Fig. A1. The differences used for the calibration were mostly within the expanded uncertainty (0.4×10^{-3} in practical salinity), although the differences for the older batches sometimes deviated outside the expanded uncertainty.

APPENDIX B

Time Drift of the Salinometer

Time drift of the salinometer was estimated from ultrapure water (Milli-Q water from MilliporeSigma) and the IAPSO SSW measurements at the beginning and the end of the seawater sample measurements for each day during the R/V *Mirai* cruise MR19-04 (Fig. B1). The salinometer drifted in time probably because of the contribution from the conductivity cell, because the salinometer was electrically stable during the cruise; the standard

FIG. A1. Differences in practical salinity from the batch-to-batch offset-corrected value (see Table A1). Closed circles show the differences that were used for the calibrations (bottle ID “R” in Table A1), and open circles show the differences that were simultaneously measured at the determination of the batch-to-batch offset of a target batch but not used for the calibration (ID “N” in Table A1). Dashed lines show the expanded uncertainty of the label salinity (Bacon et al. 2007).

deviation of the readings with the FUNCTION switch on both of ZERO and STANDBY was smaller than one last digit (see the technical manual for the salinometer; Guildline Instruments 2004). The salinometer was stable for the first half of the cruise but drifted (about -0.0012 in practical salinity per 22 days for SSW measurements) for the second half of the cruise by changing the span of the slope (Fig. B1).

The measurement of a batch-to-batch offset estimation for five consecutive batches (a total of 25 bottles) takes 3 h or less. Therefore, the effect of time drift of the salinometer on the batch-to-batch offset estimation is generally small and is negligible by calibrating the salinometer as shown in Fig. 1.

APPENDIX C

Repeatability of the Decade Resistance Substituter Measurements

The uncertainty of the HARS decade resistance substituter is claimed by the manufacturer to be $\pm(0.01\% + 2 \text{ m}\Omega)$. If there is no correlation between the uncertainty of $R_{2,0}$ and R in the calculation of Eq. (1), then the uncertainty of $2R_{2,0}/R$ can be estimated from

FIG. B1. Time series of the measured double conductivity ratios $2K$ for (a) the ultrapure water and (b) the IAPSO SSW (batch P162). Dashed lines indicate the average for the ultrapure water and double the label conductivity ratio for the IAPSO SSW. The regression line for the IAPSO SSW measurements (days from 27 to 51) is also shown.

FIG. C1. Linearity errors in practical salinity estimated from measurements of the decade resistance substituter (serial No. E1-13514822) for salinometers with serial Nos. (a) 62556 and (b) 62827. The decade resistance substituter was calibrated by the manufacturer in December 2013 (IET Laboratories, Inc.). The errors were evaluated five or seven times over two or four years for each salinometer.

$$U = 2R_{2.0}/R(r_{2.0}^2/R_{2.0}^2 + r^2/R^2)^{0.5}, \quad (\text{C1})$$

where $r_{2.0}$ is the uncertainty of $R_{2.0}$ and r is the uncertainty of R . U is about 0.0003 (0.006 in practical salinity) and 0.0001 (0.00015 in practical salinity) for $2R_{2.0}/R$ of 2 and 0.1, respectively. However, $r_{2.0}$ and r are correlated. For example, U must be zero when R is equal to $R_{2.0}$. Therefore, U must be smaller than these estimates, although the resistance of the decade resistance substituter might drift over time. In fact, the results of the decade resistance substituter measurements repeated over two or four years agree well with each other, and the variability is nearly within the resolution of the salinometer ($\pm 0.2 \times 10^{-3}$ in practical salinity) (Fig. C1).

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