Testing a new quick response oxygen sensor, “RINKO”

by

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Abstract

We evaluated a new quick response dissolved oxygen (DO) sensor “RINKO”, currently under development by JFE Advantech Co., Ltd., to determine its in situ response and applicability to hydrographic and hydrochemical observations in the western North Pacific and in the Sea of Japan. The response time of the RINKO sensor to ambient DO changes was demonstrated at about 1 s in these in situ experiments. RINKO data were calibrated to temperature, pressure, and bottle sample DO data obtained by conventional Winkler method, yielding a precision of < ± 1 μmol kg⁻¹, except in the upper layers of the ocean where vertical DO variations are large. Although the sensor was subject to instrumental drift during the period of a cruise (equivalent to < 6 μmol kg⁻¹ DO) and to pressure hysteresis between downcasts and upcasts (< 4 μmol kg⁻¹), the RINKO sensor is capable of observing continuous vertical DO profiles with a precision that is sufficient for most practical purposes. The RINKO sensor will contribute to an improved understanding of DO variability, providing an expanded DO database with enhanced spatial and temporal resolution.

1. Introduction

Dissolved oxygen (DO) is a fundamental biogeochemical parameter in oceanic systems, reflecting biological activity, air–sea interactions and oceanic circulation. In the ocean interior, changes in DO are closely related to changes in other biogeochemical parameters, such as nitrate, phosphate, and dissolved inorganic carbon (DIC). The inverse relationship between DO and DIC is of particular importance; in the euphotic zone, DO is produced (and DIC consumed) as a consequence of photosynthesis and is consumed (and DIC produced) by the respiratory processes of autotrophic and heterotrophic organisms. Therefore, observations of DO in the ocean are crucial for discriminating changes in ocean carbon content due to the increase in anthropogenic CO₂ from those due to biological activity and/or ocean circulation (e.g., Gruber, 1998).

Concentrations of DO in seawater in a discrete sample bottle have been determined using a titration technique developed by Winkler (1888); because DO concentrations can be determined with high precision (< 1 μmol kg⁻¹) with this relatively simple method, it has been widely used for oceanographic observations, and is the basis for a large, good quality, historical DO database. However, an inherent disadvantage of titration methods using discrete sampling bottles is that the resulting data inevitably represent rather sparse sampling intervals, both spatially and temporally.

DO sensors are another powerful tool for determination of DO concentrations in seawater. DO sensors allow continuous automated observations and thus the determination of DO variability in great detail. Recently, Argo floats with attached DO sensors have been deployed in the oceans, thus facilitating the collection of high spatial and temporal density datasets in space and time (Gruber et al., 2007; Körtzinger et al., 2008).

Several types of DO sensors have been developed. The SBE-43 (SeaBird Electronics Inc.) is commonly used for hydrochemical observations because the instrument has a quick response time (< 7 s at 29.2°C and < 28 s at 1.7°C, for a 99% nominal response); however, it is subject to long-term instability and pressure hysteresis. The Aanderaa optode (Aanderaa Data Instruments AS) is another widely used sensor, exhibiting excellent temporal stability and suitability for mooring observations; however, the sensor is less suitable...
for hydrochemical observations because its response time is slow relative to the DO change during the CTD’s motion (Uchida et al., 2008). Appropriate calibration can largely compensate for the limitations of the SBE-43 and Aanderaa optode sensors (Uchida et al., 2010). However, the response time of DO sensors in response to rapidly changing DO concentrations is critical for collection of shipboard vertical hydrographic and hydrochemical observations using CTD systems, because the quick response yields high resolution data that clarify the detailed structure of vertical DO profiles.

Recently, a new optical DO sensor, “RINKO” (JFE Advantech Co., Ltd.), was developed on the basis of fluorescence quenching of a pressure sensitive paint layer. The RINKO sensor is outstanding for its quick response time to changes in DO concentrations (< 1 s, 90% response at 25 °C, according to the manufacturer’s specifications), and is therefore considered applicable for continuous and highly accurate shipboard vertical observations in conjunction with CTD measurements. RINKO sensors have already been used for basin-scale hydrographic observations (Murata et al., 2009), and Uchida et al. (2010) have proposed a sophisticated calibration procedure. However, information on the performance of RINKO sensors is still insufficient to identify its constraints and full range of applications; further studies are required to suggest improvements to the RINKO sensor system. In this study, we used RINKO for shipboard hydrographic observations in the subarctic to subtropical western North Pacific and in the Sea of Japan. On the basis of the results, we evaluated RINKO’s performance and have proposed a simple calibration procedure for convenient use in hydrographic observations.

2. Materials

A series of experiments with a RINKO sensor in conjunction with a CTD system were conducted on board the RVs Ryofu-maru, Keifu-maru, and Seifu-maru of the Japan Meteorological Agency (JMA) between April and June 2009 in the western North Pacific and in the Sea of Japan (Table 1, Fig. 1). The RINKO sensor (RINKO-III, JFE Advantech Co., Ltd.) was connected to the CTD system (SBE 911plus, Sea-Bird Electronics, Inc.) with a carousel multi-sampler. RINKO and CTD data were processed and acquired at a vertical interval of 1 dbar (JMA, 1999). The pressure data were filtered by using a low pass filter with a time constant of 0.15 s, as recommended by SBE. Temperature and salinity data were obtained by the CTD sensor. Raw RINKO output was converted to percent oxygen saturation by DO Converter software (JFE Advantech Co., Ltd.), which uses an algorithm based on inputs of raw RINKO data, temperature, and pressure. DO concentrations (μmol kg⁻¹) were then calculated as the product of the percent oxygen saturation and the oxygen

Table 1. Japan Meteorological Agency cruises on which RINKO sensors were tested.

<table>
<thead>
<tr>
<th>Ship</th>
<th>Cruise</th>
<th>Date</th>
<th>Area</th>
<th>CTD stations without bottle samplings</th>
<th>CTD stations with bottle samplings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ryofu-maru</td>
<td>RF09-04</td>
<td>22 April – 12 May 2009</td>
<td>south of the Kuroshio – the Kuroshio – Oyashio Transition Zone</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>Keifu-maru</td>
<td>KS09-04</td>
<td>23 April – 13 May 2009</td>
<td>western North Pacific (137°E)</td>
<td>8</td>
<td>25</td>
</tr>
<tr>
<td>Seifu-maru</td>
<td>SM09-04</td>
<td>24 April – 8 June 2009</td>
<td>Sea of Japan</td>
<td>5</td>
<td>74</td>
</tr>
</tbody>
</table>

*Only upper water layers (pressures < 2000 dbar) were observed at the last 18 stations*
solubility (Garcia and Gordon, 1992). To assess the response time of RINKO sensors, we sampled the serial output of the CTD and RINKO sensor data (24 Hz; 0.0417 s) to create datasets representing output streams at three frequencies: (1) the first dataset represents an 8-Hz frequency (0.125-s), chosen to approximately correspond with the sampling rates of the RINKO sensor (ca. 10 Hz), reflecting high frequency (short interval) data acquisition; (2) the second dataset represents 1-s output intervals, chosen to evaluate the rate of change in each 1-s; (3) the third dataset represents 7-s running averages calculated from (2), chosen to smooth out fluctuations associated with the frequency of the ship’s roll (5—9-s cycle).

At hydrographic/hydrochemical stations, the CTD underwater unit was winched down (downcast) into the sea at a speed of ca. 0.8 m s\(^{-1}\) to the maximum depth of observation; the unit was then winched up (upcast) at a speed of ca. 1.0 m s\(^{-1}\), while stopping at sampling depths to enclose water samples in Niskin bottles mounted to the carousel multisampler. To collect the water samples, the upcast speed of the unit was gradually decreased over a depth interval corresponding to ca. 10 dbar; the unit was stopped for about 20 s at each sampling depth to close the bottle.

After the CTD unit arrived on deck, the Niskin bottles were sub-sampled into precalibrated glass bottles for DO analyses by a modified Winkler method (Carpenter, 1965). The repeatability of measurements inferred from replicate analyses was 0.35 μmol kg\(^{-1}\) (n = 23).

3. Results and discussion

3.1. Rapid response of the RINKO sensor

Rapid response time is a key property of sensors designed to obtain precise measurements in variable environments. To evaluate the in situ response time of the RINKO sensor, we examined the rate of change of RINKO output at hydrographic stations showing large depth-related DO variations. One such station (RF-3369; 37°N, 147°E) in the Kuroshio–Oyashio Transition Zone was observed in April 2009 during the RV Ryofu-maru’s RF09-04 cruise. Within the upper layer at this station, calibrated RINKO DO (see next section) showed large and rapidly changing depth-dependent variations in DO concentrations: 140–268 μmol kg\(^{-1}\) at pressures of 280–150 dbar, and 206–283 μmol kg\(^{-1}\) at pressures of 50–25 dbar; these variations are related to horizontal advection of the Kuroshio current (low DO and saline water) and the Oyashio current (high DO and fresh water) (Fig. 2). At this station, the CTD underwater unit was stopped on the upcast for about 20 s at pressures of 500, 400, 300, 250, 200, 150, 125, 100, 75, 50, 25, and 10 dbar (see horizontal steps in the thick gray line, Fig. 3a) to collect water samples in Niskin bottles. We examined the rates of change of pressure, raw RINKO output, and RINKO DO concentration using a 7-s running average of the data resampled at 1-s intervals. The rate of pressure change was approximately −1 dbar s\(^{-1}\), except when the CTD underwater unit was stopped to collect water samples (thick gray line, Fig. 3b). In regions with steep DO gradients, the rate of change of raw RINKO output and calibrated RINKO DO values (thin and thick black lines, respectively, Fig. 3b) showed large time-dependent variations, with rates of change of DO concentration of up to 7 μmol kg\(^{-1}\) s\(^{-1}\) (data sampled at 1-s intervals); the calibrated RINKO DO closely track the pressure change variations, without showing any marked delays in response to the pressure changes associated with deceleration or acceleration of the CTD underwater unit when the upcast was paused for sampling (Fig. 3b). When the CTD underwater unit stopped ascending at 50 dbar (approximately 100 s before the end of observations), the DO concentration decreased sharply and the rate of change in the raw RINKO output and the calibrated RINKO DO showed a slight delay relative to the pressure. However, the CTD temperature measurement, with response time nominally 0.065 s, also showed a similar delay and the temperature–pressure relationship was also changed.
at this time (data not shown). This suggests that the raw RINKO output delay was not due to a delay in response but was likely caused by spatial DO variations.

To assess the response of the RINKO sensor in more detail, we examined data at 8-Hz frequencies (0.125-s intervals) in the vicinity of the 400-dbar depth, where the CTD underwater unit stopped ascending for about 40 s and the variability of DO gradient was small (Fig. 4). The raw RINKO output and pressure data show approximately syn-chronous fluctuations, but the raw RINKO output shows a phase delay relative to pressure; note that the pressure sensor is considered temporally more stable because its response time (nominally 0.015 s) is much faster than that of the RINKO sensor (manufacturer specifications: <1 s for 90% response at 25°C). To compare the in situ response time of the RINKO sensor with that of the pressure sensor, the lag correlations between the raw RINKO output and pressure data were examined using a dataset with an 8-Hz frequency (0.125-s sample interval). The lag correlation, plotted as a function of lag time (Fig. 5), shows smoothly fluctuating
variations with a peak lag correlation at approximately 1 s (average temperature was 4.7°C) and a period (ca. 7 s) corresponding with the ship’s roll (5−9 s). This result indicates that the in situ response time of the RINKO sensor to ambient DO changes is approximately 1 s at 4.7°C, which is comparable to the manufacturer’s specifications derived from laboratory tests (< 1 s for 90% response at 25°C).

3.2. In-situ RINKO sensor calibration
RINKO DO concentrations calculated using the algorithm provided by the manufacturer (hereinafter RINKO-DO) systematically differed from values obtained directly using the Winkler method (hereinafter Winkler-DO). The differences between RINKO-DO and Winkler-DO values were depth-dependent and were particularly large at pressures less than 1000 dbar where DO and temperature were highly variable (Fig. 6). In contrast, differences between RINKO-DO and Winkler DO values at pressures greater than 1000 dbar were relatively small, and showed systematic variations with depth. In addition, the magnitude of the differences gradually changed during the course of each cruise, indicating that the RINKO sensor is subject to instrumental drift and requires periodic calibration to obtain precise measurements.

We attempted to calibrate the RINKO sensor using in situ Winkler-DO data, first using a quadratic regression of Winkler-DO values against corresponding RINKO-DO values (open circles, Fig. 7). Adding the first-order terms for temperature ($T$) and pressure ($P$) values to the quadratic...
expression for RINKO-DO yielded a corrected RINKO-DO estimate (hereinafter corRINKO$_0$-DO), given by
\[
\text{corRINKO}_0\text{-DO} = a \times \text{RINKO-DO}^2 + b \times \text{RINKO-DO} + c \times T + d \times P + e,
\]
where a, b, c, d, and e are coefficients. DO values calculated on the basis of the calibration showed a strong correspondence with Winkler-DO values, as represented by the 1:1 correspondence between corRINKO$_0$-DO and Winkler-DO (closed circles, Fig. 7). The multiple regression compensates for nonlinear changes in raw RINKO output in response to ambient oxygen saturation and for dependence to ambient temperature, and pressure.

Using the above calibration equations, differences between corRINKO$_0$-DO and Winkler-DO values were mostly reduced to $< \pm 5 \mu\text{mol kg}^{-1}$. However, the targeted difference between RINKO and Winkler DO values ($< \pm 1 \mu\text{mol kg}^{-1}$) was not achieved. Furthermore, the magnitude of the differences changed with time ($< 6 \mu\text{mol kg}^{-1}$) during the course of a cruise because of instrument drift (Fig. 8); this could not be corrected using a single set of coefficients for the period of a cruise. It was difficult to estimate the magnitude and persistence of instrument drift because the drift varied during different cruises. However, we observed that the magnitude of instrument drift was less towards the end of a long cruise (Fig. 8c), suggesting that the RINKO sensor might stabilize during long-term use.

We next attempted to calibrate the RINKO DO values for each sampling cast to remove the biases caused by instrument drift (hereinafter corRINKO-DO), by incorporating time-dependent changes in the values of the regression coefficients in the quadratic multiple regression equation (Fig. 9; data for cruise RF09-04). The variations in the coefficients during the course of the cruise were relatively small. However, by calibrating the RINKO data to the Winkler data for each hydrocast, differences between corRINKO-DO and Winkler-DO were mostly reduced to $< \pm 1 \mu\text{mol kg}^{-1}$ over the water columns from near-surface to deep layers at ca. 6000 dbar (Fig. 10).

During the cruises, bottle samples were collected at least every few sampling stations, and at least once a day. For stations with no bottle sampling, RINKO DO values were calibrated to Winkler-DO data by using both preceding and succeeding sampling stations, since the RINKO-DO drift between neighboring sampling stations was expected to be $< \pm 1 \mu\text{mol kg}^{-1}$ (Fig. 8). The values of the calibration coefficients for stations without bottle-sampling were usually the values of preceding and succeeding sampling stations (Fig. 9).

Despite the corrections, large discrepancies ($> \pm 3 \mu\text{mol kg}^{-1}$) between corRINKO-DO and Winkler-DO were sometimes observed in the upper layers, especially in the Kuroshio−Oyashio Transition Zone (Fig. 10a and b). It is likely that these large discrepancies can be attributed to large variations in DO concentrations with depth. In the Kuroshio−Oyashio
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Transition Zone, vertical DO profiles showed DO-depth gradients that exceeded 10 μmol kg\(^{-1}\) dbar\(^{-1}\) at a pressure of approximately 50 dbar (Fig. 2). If the CTD underwater unit was stopped at a depth corresponding to a large DO gradient, the differences between RINKO-DO and Winkler-DO data might be attributed to the physical distance between the RINKO sensor and the Niskin bottles, which was more than a few tens of centimeters vertically. Reducing this difference in the upper layers is difficult, especially in the area where the DO profile is largely variable.

Finally, it is possible that some large discrepancies between corRINKO-DO and Winkler-DO data observed in both shallow and deep water layers were caused by sampling errors or analytical errors in the Winkler method. If an error in the Winkler-DO value is suspected, the data should be carefully compared with the RINKO-DO profile, as the RINKO-DO data may be helpful for detecting such errors.

3.3. Pressure hysteresis

In the previous section, we demonstrated that high-precision RINKO sensor calibration (< ± 1 μmol kg\(^{-1}\)) at a sampling station can be achieved by using DO data from bottle samples analyzed with the Winkler titration. However, the bottle samples are generally collected on the upcasts, and we were not certain whether output of the RINKO sensor would vary depending on its direction of motion (descent versus ascent). To determine whether the RINKO sensor was properly calibrated for downcasts, we examined the differences between vertical corRINKO-DO profiles obtained on downcasts and upcasts in deep layers where the vertical DO gradient was gentle and temporal variability is expected to be negligible.

Data from all three cruises showed that corRINKO-DO values from downcasts were systematically larger than those from upcasts; in deep layers, the differences were up to 4 μmol kg\(^{-1}\) (Fig. 11). The greater the maximum pressure on a hydrocast, the greater the magnitude of the differences between the corRINKO-DO values from downcasts and upcasts (Fig. 11a, c, and e), indicating that the differences were dependent on the magnitude of the maximum pressure.
in each cast and were probably not artifacts of pressures encountered in previous casts. Even on shallower casts in which the maximum observed pressure was only about 2000 dbar at the last 18 stations on KS09-04, the differences were still not negligible (Fig. 11c). In addition, in the Sea of Japan (cruise SM09-04; Fig. 11e and f) where DO concentrations were essentially constant (Winkler-DO variations were less than 4 μmol kg\(^{-1}\)) at pressures greater than about 2000 dbar (corresponding to the Japan Sea Proper Water, JSPW; Fig. 11f), the upcast–downcast differences in deep layers changed almost linearly with pressure (Fig. 11e), suggesting that the differences are primarily dependent on pressure and change almost linearly under conditions where DO concentrations are constant.

Although the differences in the upper layers might be partly attributable to spatial and temporal DO variability, these systematic differences indicate that the RINKO sensor is subject to pressure-induced time-dependent memory effects (i.e., pressure hysteresis) that cause output differences between descending (pressurizing) and ascending (depressurizing) casts. Because RINKO sensor output from downcasts was not calibrated with DO data from bottle samples, the downcast data should be used with caution. Note, however, that the response of the RINKO sensor to ambient DO varia-

![Fig. 10](image-url)
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RINKO DO data obtained on the downcast was chosen such that the potential density matched that of bottles sampled on the upcast. However, at pressures greater than 2000 dbar, the resulting corRINKO-DO values obtained using downcast data had a somewhat larger uncertainty (< ± 4 μmol kg⁻¹) than values obtained on the upcast (Fig. 12). At pressures less than 2000 dbar, the uncertainty of corRINKO-DO values on the downcast was even greater than that for values obtained on the upcast. Because the vertical structure of the upper layer during downcasts was not necessarily the same as the structure during upcasts, the calibration on downcasts using bottle data obtained on upcasts might generate unreliable results.

Uchida et al. (2010) present a sophisticated algorithm for RINKO sensor calibration that gives accurate DO profiles on both downcasts and upcasts. Their algorithm is most helpful when the DO profile is merged with CTD data from
downcasts (as are usually reported). However, the relatively simple method described above facilitates the collection of DO profiles obtained on the upcast with precisions \(< \pm 1 \mu\text{mol kg}^{-1}\). Detailed DO profiles acquired on the upcast are important because other biogeochemical parameters closely coupled with DO concentrations (e.g., nutrient, CO\(_2\) system parameters, dissolved organic carbon, etc.) can only be obtained by bottle sampling on the upcast. We suggest that CTD and RINKO data be reported not only from downcasts but also from upcasts, in order to give DO results that can be compared with data for other biogeochemical parameters obtained on the upcast.

4. Conclusion

A new quick response DO sensor (RINKO) developed by JFE Advantech Co., Ltd., was mounted on a CTD system. With this sensor, we successfully obtained high quality DO data from shipboard hydrographic and hydrochemical observations in the western North Pacific and in the Sea of Japan.

Our results demonstrated that the RINKO sensor responds to ambient DO changes within about 1 s, which compares favorably with the manufacturer’s specifications. Although DO values calculated using the manufacturer’s algorithm are biased in comparison with bottle sample DO data, and some problems such as instrument drift and pressure hysteresis were identified, these issues could mostly be corrected by calibrating the instrument with a multiple regression equation with CTD temperature and pressure data and DO values obtained by bottle sampling and Winkler titration analyses on the upcast. Using this method, we were able to obtain continuous reliable high precision DO data (\(< \pm 1 \mu\text{mol kg}^{-1}\)) in most environments, except where DO concentrations change rapidly with depth. When the RINKO sensor is further improved and the problem of instrument drift is resolved, it will be possible to use Winkler-DO data from multiple sampling stations within a certain time interval or leg of the cruise to calibrate the RINKO-DO within the targeted resolution of less than 1 \(\mu\text{mol kg}^{-1}\).

The instrument’s quick response is the RINKO sensor’s main advantage over other DO observation instruments, and our results confirmed the RINKO sensor’s superior performance as a DO observation instrument. Application of the RINKO sensor to oceanographic observations will clarify and provide details about the vertical structures of DO concentrations, which are difficult to detect with CTD sensor and other sensors. Full utilization and application of the RINKO sensor will contribute to our understanding of DO variability.

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References


高速応答 DO センサー RINKO の検証

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JFE アドバンテックが新たに開発した高速応答溶解酸素 (DO) センサー RINKO を多筒採水器付 CTD システムに搭載し、西部北太平洋および日本海において各層観測を行った。現場での観測によって、RINKO は DO の変化に対して素早く応答することが確かめられた。RINKO の出力には、時間ドリフト (< 6 µmol kg⁻¹) や、下げと上げのキャストの間で圧力ヒステリシス (< 4 µmol kg⁻¹) の問題がみられたが、各層観測による DO ボトルデータに加えて、水温や圧力のデータを用いて補正することができた。DO の変動が鉛直的に大きい表層を除き、今回の場合によって RINKO から得られた DO の不確かな 1 µmol kg⁻¹ 以内であった。このように RINKO は CTD システムと共に使用する上で対面的に十分な精度で鉛直的に連続して DO を観測することが可能であり、より詳細な DO の時間・空間的変動の把握に大いに役立つであろう。