https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

Biogeosciences
Discussions
Open Access
EGU

Acidification-vulnerable carbonate system of the East Sea (Japan Sea)

Taehee Na[1], Jeomshik Hwang[1*], Soyun Kim[2], Seonghee Jeong[2], TaeKeun Rho[3], Tongsup Lee[2]

1 School of Earth and Environmental Sciences/Research Institute of Oceanography, Seoul National University, Seoul 08826, Republic of Korea

2 Department of Oceanography, Pusan National University, Busan 46241, Republic of Korea

3 Korea Institute of Ocean Science and Technology, Busan 49111, Republic of Korea

* corresponding author

jeomshik@snu.ac.kr

School of Earth and Environmental Sciences, Seoul National University, Seoul 08826, Republic of Korea

Manuscript prepared for *Biogeosciences*

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

Biogeosciences
Discussions
Open Access
EGU

Abstract

The East Sea (Japan Sea) has its own deep overturning circulation, but this operates over a much shorter timescale than that in the open ocean. This allows the East Sea to be used as a natural laboratory in which to investigate potential future changes in the oceanic system. Dissolved inorganic carbon (DIC) and total alkalinity (TA) were measured in 2014 and 2017 to investigate the characteristics and temporal variability of the carbonate system of the East Sea. When the East Sea was compared with a site in the South Atlantic that has similar apparent oxygen utilization (AOU) values, it was also found to have similar DIC content of the deep waters. However, the TA levels in the East Sea were much lower than those recorded in the South Atlantic. Consequently, the DIC/TA ratio of the deep waters of the East Sea was high and similar to that in the North Pacific, which leaves the deep waters of the East Sea vulnerable to acidification by CO_2 input. High export production of organic matter, together with low rates of $CaCO_3$ export, are responsible for this high DIC/TA ratio. In the Ulleung Basin, in the southwest of the East Sea, the DIC and AOU of the deep waters increased between 1999 and 2014. pH decrease of the deep waters and shoaling of the carbonate saturation horizons was faster than that recorded in the oceans. Both slowed deep-water ventilation, and the intrusion of anthropogenic CO_2 contributed to the acidification of the East Sea. However, a clear increase in DIC from the Japan Basin to the Ulleung Basin, accompanied by a commensurate increase in AOU, was observed in 2014, whereas the meridional gradient was absent in 1999. This observation appears to reflect recent changes in deep-water ventilation, such as the re-initiation of deep-water formation. The East Sea is

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

extremely vulnerable to acidification and should be seen as a special case of ocean acidification rather than an example of how the oceans will respond to a slowdown in ventilation in the future.

Keywords:
dissolved inorganic carbon, acidification, carbonate saturation horizon, deep-water ventilation

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

1. Introduction

The East Sea (also known as the Japan Sea and referred to as the ES hereafter) is a semi-enclosed marginal sea in the northwest Pacific, and is surrounded by the Korean Peninsula, Russia, and the Japanese islands (Fig. 1). The ES has an average depth of 1350 m and is connected to the Pacific through three shallow straits (depth < 150 m). It contains three basins: the Japan Basin in the north, the Ulleung Basin in the southwest, and the Yamato Basin in the southeast. The ES has ocean-like deep-water formation and a meridional circulation, which is isolated from the Pacific (Senjyu and Sudo, 1993; Kawamura and Wu, 1998; Kim et al., 2002; Talley et al., 2003). Deep-water ventilation in the ES has a much shorter timescale, of hundreds of years, than that seen in the open ocean (Tsunogai et al., 1993; Kim and Kim, 1996; Kumamoto et al., 1998). Consequently, the ES has the potential to act as a 'natural laboratory' that can be used to examine more easily how changes occur in the open ocean (Kim and Kim, 2001).

A number of studies have investigated the carbonate system of the ES. The first systematic survey of CO_2 parameters in 1992 showed that the nTA (total alkalinity normalized to a salinity of 35) and nDIC (total dissolved inorganic carbon normalized to a salinity of 35) values were lower than those of the Pacific (Chen et al., 1995). Park et al. (2006, 2008) proposed a large uptake of atmospheric CO_2 by the ES from 1992 to 1999 and subsequent decrease in the CO_2 absorption rate from 1999 to 2007 (from 0.6±0.4 to 0.3±0.4 mol C $m^{-2}yr^{-1}$). The shoaling of the carbonate saturation horizons was reported by Park et al. (2006). Kim et al. (2014) found rapid acidification since 1995 (i.e., a decrease in pH of

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

68 0.03±0.02 pH units decade^{-1}) in the surface waters of the Ulleung Basin.

69 Recently, Chen et al. (2017) estimated pH from long-term measurements of the
70 dissolved oxygen (DO) concentration and showed a rapid decrease in pH in the interior of the
71 ES. They suggested that this rapid decrease was caused by the accumulation of CO_2 supplied
72 from organic matter decomposition, which was facilitated by the slowdown of deep-water
73 ventilation. Furthermore, rapid acidification of the interior of the ES was projected for the
74 near future based on the empirical temporal trend in pH (Chen et al., 2017). However, this
75 projection was made under an assumption of continued ventilation slowdown and needs to be
76 evaluated based on monitoring of the carbonate system and DO as well as the deep-water
77 ventilation.

78 In this study we report the concentrations of CO_2 parameters measured in 2014 and
79 2017 in the ES. The characteristics of the carbonate chemistry of the ES were investigated by
80 focusing on the similarities and differences relative to the system in the ocean. Also, we
81 investigated the spatial and temporal variations of the CO_2 parameters in the ES and their
82 implications for the deep-water circulation and future changes in the carbon cycle of the
83 ocean.

84

85 **2. Methods**

86 Seawater samples for DIC and TA analysis were collected during April 2014, along a north–
87 south transect through the ES from the R/V *Akademik Lavrentyev*, and also during May 2017,
88 but this time only in the Ulleung Basin, from the survey ship *Haeyang 2000* (Fig. 1). Samples

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

were collected in 600-ml boro-silicate glass bottles and a 200-µl saturated $HgCl_2$ solution was then added following the standard protocol of Dickson et al. (2007). DIC and TA were measured in a land-based laboratory using a VINDTA 3C (Marianda, Germany) by coulometric titration and potentiometric titration, respectively. The measurement precision was ±2 µmol kg^{-1} for both DIC and TA. A standard material, provided by A. Dickson at the Scripps Institution of Oceanography, USA, was analyzed frequently, including each time a new titration cell was installed. The DIC and TA results obtained from the standard were within ±2 µmol kg^{-1} of the reported values. The results are provided in Table S1.

Measurements of pH (n = 59) were made on board during the 2014 cruise. pH was measured spectrophotometrically by addition of m-cresol purple after temperature adjustment to 25°C (Clayoton and Byrne, 1993). pH values measured at 25°C were converted to values at the in situ temperature and pressure. For the 2014 cruise, when three parameters were measured, the measured pH values and those calculated from DIC and TA were compared. Calculated pH values were higher than the measured values by 0.039 on average (n = 22) at pH values > 8. Values lower than 8 were similar (average difference was −0.02 ± 0.027 with the calculated values being higher, n = 37). Values > 8 were observed mainly in the surface water. For the 2017 cruise, pH was not measured and instead was estimated from the DIC and TA measurements using CO2SYS (Lewis and Wallace, 1998). The saturation states of calcite and aragonite, Ω_{calc} and Ω_{arag}, respectively, were calculated using CO2SYS (Dickson and Millero, 1987; Mehrbach et al., 1973). Temperature and salinity were measured using a CTD

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

(SBE 9 plus). DO was measured using either Winkler titration or a sensor (SBE 43) with calibration by Winkler titration.

We compared our data with those from previous studies completed in 1992 (Chen et al., 1995) and 1999 (TA and pH were measured and DIC was calculated; Talley et al., 2004). Oceanic data for comparison were obtained from the GLODAP version 2 (Global Ocean Data Analysis Project version 2; https://www.nodc.noaa.gov/ocads/oceans/GLODAPv2/; Key et al., 2016; Olsen et al., 2016).

Stations were renamed for convenience to include the sampling year and their location abbreviated to JB (i.e., Japan Basin), UB (i.e., Ulleung Basin), or KP (i.e., the region in between, close to the Korea Plateau). Stations 99-JB, 99-KP, and 99-UB were originally Stations 187, 181, and 120, respectively (Talley et al., 2004). Stations 14-JB, 14-KP, and 14-UB were originally Stations M13-2, M8, and M4, respectively. Station 17-UB was originally Station OF3-5.

3. Results

3.1. Vertical distribution of CO_2 parameters

In the ES, potential temperature and salinity typically vary within the upper 500 m, but below this upper layer the values are uniform, falling within ±0.1°C in temperature and ±0.002 in salinity (not shown). The deep interior is occupied by Central Water, Deep Water, and Bottom Water (Kim et al., 2004). Currently, the boundary between Central Water and Deep Water, defined by the 0.13–0.15°C isotherm, lies at depths of between 1400 and 1800 m (Yoon et al.,

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

2018). The boundary between Deep Water and Bottom Water lies at around 2500 m. However, as the values of the CO_2 parameters vary little, for convenience, we will refer to these water masses as 'deep waters' in this paper. In the Ulleung Basin, intermediate water (Japan/East Sea Intermediate Water, JESIW; Yoon and Kawamura, 2002) occupies the 200–400 m layer, below the Tsushima Warm Current.

In both 2014 and 2017, the DO concentration generally decreased with increasing depth; however, in the Japan Basin, DO increased slightly with increasing depth below approximately 1000 m (Fig. 2a). Values in the Japan Basin were much higher than those in the Ulleung Basin. The apparent oxygen utilization (AOU) showed a monotonic increase with increasing depth up to about 160 μmol kg^{-1} in the Ulleung Basin (Fig. 2b). DIC increased sharply with depth, from about 2000 to about 2230 μmol kg^{-1}, in the upper 500 m (Fig. 2c). Below around 1000 m, DIC ranged between 2230 and 2260 μmol kg^{-1}. TA ranged between 2250 and 2290 μmol kg^{-1} in the upper 500 m (Fig. 2d). TA and salinity showed a positive correlation (TA = 63 × salinity + 110; R^2 = 0.80, n = 120) in the upper 500 m. Below 500 m, TA showed a general increase with increasing depth.

3.2. Meridional variation in DIC and AOU in the deep waters

Conveyor-belt-like deep water circulation can generate a meridional gradient in properties such as DIC and AOU. We examined the data at depths below 1000 m by binning the sites into three regions: the Japan Basin (ca. 41°N), the Ulleung Basin (ca. 37°N), and the region in between (38–39°N; Fig. 1). Both DIC and AOU showed no meridional difference in 1999

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

(Figure S1, upper panels; Talley et al., 2004). However, in 2014, there was a large difference in AOU between the Ulleung Basin and the Japan Basin, with the Ulleung Basin values being much higher (Fig. 2 and Fig. S1, lower panels). For DIC, an increasing trend from the Japan Basin towards the Ulleung Basin was observed in 2014 (Fig. 2). The difference between the Japan and Ulleung basins, averaged over the water column below 1000 m, was approximately 12 and 23 μmol kg^{-1} for DIC and AOU, respectively. The trend in TA was not clear, although the values in the Japan Basin were generally lower than at the other sites.

3.3. Temporal variations in DIC and AOU in the Ulleung Basin

We compared our data with previously published data from the Ulleung Basin, where data coverage was the longest. We examined the results from the layer between 500 and 1000 m, and also that between 1000 m and the bottom, to focus on the variations associated with deep-water ventilation (Fig. 3). AOU increased by approximately 25 μmol kg^{-1} from 1992 to 1999, but only slightly from 1999 to 2014 in the 500–1000 m layer. In comparison, in the deeper layer, AOU increased slightly from 1992 to 1999, but by around 23 μmol kg^{-1} from 1999 to 2014. DIC did not change, or decreased slightly, from 1992 to 1999, but then increased considerably from 1999 to 2014 in both layers. pH did not change from 1992 to 1999, but decreased from 1999 to 2014. No significant changes were observed for AOU, DIC, and pH between 2014 and 2017. Our observed values were generally in fair agreement with the trend reported by Chen et al. (2017).

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

171 The Ω_{calc} and Ω_{arag} values decreased clearly in the Japan Basin from 1999 to 2014
172 (Fig. S2). However, they showed no clear trend in the upper 500 m in the Ulleung Basin. The
173 calcite saturation horizon shoaled from around 1300 m in 1992 to about 500 m in 2014 (Fig.
174 4). In contrast, the aragonite saturation horizon shoaled from about 500 m in 1992 to 300 m
175 in 1999, after which time it did not shoal further in 2014 and 2017 (Fig. 4).
176
177 **4. Discussion**
178 **4.1. Characteristics of the East Sea carbonate system**
179 The characteristics of the carbonate system in the ES were revealed by a comparison with
180 that in the open ocean. For this comparison, we chose a site in the South Atlantic (St. 31;
181 47.00°S, 32.13°W; sampled in 2005; EXPCODE: 33RO20050111) where the AOU values of
182 the NADW (North Atlantic Deep Water) layer are similar to those in the ES, and also sites at
183 similar latitudes in the North Atlantic (St. 191; 31.95°N, 26.26°W; sampled in 2004;
184 EXPCODE: 06MT20040289) and North Pacific (St. 71; 37.98°N, 166.46°E; sampled in 2012;
185 EXPCODE: 49RY20120726) (Fig. S3). The increase in nDIC from the surface of the North
186 Atlantic to the deep interior of the South Atlantic during the transit of the meridional
187 overturning circulation was approximately 290 μmol kg^{-1}, which is similar to the increase
188 from the surface water to the deep waters in the ES of around 280 μmol kg^{-1} (Fig. 5 and Fig.
189 S3b). However, nTA increased by only about 30 μmol kg^{-1} in the ES compared with 100
190 μmol kg^{-1} in the Atlantic (Fig. 5). Consequently, the DIC/TA ratio in the ES (0.988±0.002 in
191 the 1000−3000 m layer) was considerably higher than that in the South Atlantic

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

192 (0.955±0.003), and similar to that in the North Pacific (0.987±0.010) (Fig. S3d). Also, the
193 carbonate ion concentration and carbonate saturation states in the ES were similar to those in
194 the Pacific, but distinctly different from those in the South Atlantic (not shown).

195 Variations in DIC and TA levels related to organic matter decomposition and $CaCO_3$
196 dissolution are evident in the Deffeyes diagram (Fig. 5). The oceanic data show evolution
197 along the path of the meridional overturning circulation from the surface to the deep waters
198 of the North Atlantic, to the deep waters of the South Atlantic, and to the deep waters of the
199 North Pacific. In the ocean interior, the slope (i.e., nTA increase/nDIC increase) was about
200 0.85, which corresponds to contributions of 54% and 46% from organic matter
201 decomposition and $CaCO_3$ dissolution, respectively (Broecker and Peng, 1982). In the ES, an
202 increase in nTA was apparent only at depths > 500 m. The slope, 0.83, was similar to that of
203 the oceans.

204 The high rates of net primary productivity in the ES drive the high rates of DIC
205 supply of 200 g C $m^{-2}yr^{-1}$ or greater (Yamada et al., 2005; Joo et al., 2016), especially in the
206 Ulleung Basin (Kwak et al., 2013b; Joo et al., 2014). High *f*-ratio has been reported for the
207 Ulleung Basin (Kwak et al., 2013b) implying that a large fraction of organic matter
208 decomposition occurs below the euphotic layer. A sediment trap study showed that around 3%
209 of net primary production reaches a depth of 2300 m in the Ulleung Basin (Kim et al., 2017).
210 The small increase in TA can be qualitatively explained by two factors. One is the fast deep-
211 water turnover of the ES compared with the South Atlantic, which allows less time for TA
212 accumulation from $CaCO_3$ dissolution. The second factor is the small contribution from

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

213 calcifying plankton to the total plankton community (Kang et al., 2004a; Kwak et al., 2013a).
214 The average annual $CaCO_3$ flux at depths around 1000 m was 25 mg $m^{-2}d^{-1}$ (91 mmol C $m^{-2}yr^{-1}$) in the Japan Basin (Otosaka and Noriki, 2005) and 46 mg $m^{-2}d^{-1}$ (168 mmol C $m^{-2}yr^{-1}$)
216 in the Ulleung Basin (Kim et al., 2017). These values are comparable with the average values
217 in the Atlantic and Pacific (ca. 121 mmol C $m^{-2}yr^{-1}$; Honjo et al., 2008). However, because of
218 the high net primary production, the organic C to inorganic C molar ratio at 1000 m of 4.3 in
219 the Ulleung Basin (Kim et al., 2017) and 6.0 in the northeastern ES (Otosaka and Noriki,
220 2005), are considerably higher than the average values of 1.1–1.3 recorded in the Atlantic and
221 Pacific (Honjo et al., 2008).
222
223 **4.2. Meridional and temporal variation in CO_2 parameters and implication for deep-**
224 **water circulation**
225 The meridional gradient in AOU and DIC was absent in 1999 (Fig. S1, upper panels).
226 However, a southward increase was observed consistently for AOU and DIC in 2014. The
227 increase in DIC in the interior of the Ulleung Basin in excess of that in the Japan Basin is not
228 the result of anthropogenic carbon input because there is no independent deep-water
229 formation. Also, a satellite-based study observed no disproportionate change in primary
230 production between the north and south of the ES (Joo et al., 2017). A preferential increase in
231 organic matter decomposition efficiency in the Ulleung Basin compared with the Japan Basin
232 is unlikely. However, one plausible explanation is a change in deep-water circulation.

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

Our current understanding of the deep-water circulation in the ES is that there is a rather fast horizontal circulation along isopycnal surfaces with a timescale of several years (this value was obtained from simple division of the approximate path length by the deep current velocities measured by moored instruments; Senjyu et al., 2005). On top of the horizontal circulation, deep-water formation supplies oxygen-rich cold water to the interior of the northern part of the western Japan Basin (Talley et al., 2003). The meridional gradient in AOU and DIC between the Japan and Ulleung basins may become detectable under two scenarios: a significant slowdown in the horizontal circulation, or recent enhancement of deep-water formation in the Japan Basin. Under the assumption that about 10% of the net primary production of 200 g C $m^{-2}yr^{-1}$ (Yamada et al., 2005) is remineralized between depths of 500 and 2000 m in the water column, it would take approximately 10 yr for the observed increase in DIC to accumulate if organic matter decomposition was solely responsible. Based on previously published oxygen consumption rates in the ES of 3–8 μmol $kg^{-1}yr^{-1}$ (Hahm and Kim, 2008), an increase in AOU of around 20 μmol kg^{-1} would require only a few years. Therefore, a change in water circulation is a feasible mechanism with which to explain the observed meridional gradients in AOU and DIC.

Several studies have suggested a slowdown of water supply to the Bottom Water layer and increased supply to the Central Water layer instead (Kim et al., 2001; Kim et al., 2002; Kang et al., 2004b). However, a recent study reported a resumed supply of water to the Deep Water and Bottom Water layers (Yoon et al., 2018). AOU values were significantly higher in 2014 and 2017 than in 1999 in the Ulleung Basin as projected by previous studies

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

(Kang et al., 2004; Chen et al., 2017). Interestingly, in the Japan Basin, AOU values in 2014 were even lower than those in 1999, especially in the Bottom Water layer. This observation suggests that the meridional gradient was most probably caused by re-initiation of Bottom Water formation in the Japan Basin rather than a slowing of the deep-water circulation. The deep waters in the Ulleung Basin were not yet affected by the newly formed deep water as of 2014. This aspect needs to be investigated further in the future.

4.3. Acidification of deep waters

A consequence of the high DIC and low TA supply is an increase in the DIC/TA ratio in the interior of the ES (Fig. S3d). High values of DIC/TA correspond to low carbonate ion concentrations and a low pH buffer capacity. This implies that acidification by CO_2 supply from organic matter decomposition and anthropogenic CO_2 invasion could be much more serious in the interior of the ES than in the Atlantic. Indeed, the decrease in the pH of the deep waters of the Ulleung Basin is occurring much more quickly than in the open ocean (Chen et al., 2017). Shoaling of the calcite saturation horizon in the Ulleung Basin has also been occurring at a faster rate than in the ocean (e.g., Feely et al., 2012). Further shoaling, if it continues to occur, will affect calcifying organisms and may reduce $CaCO_3$ production in the future. A reduced supply of alkalinity to the deep waters makes the water more vulnerable to acidification and may form a positive feedback.

The progress of acidification should be monitored because other factors may also affect the acidification of the ES. One recently reported element of additional uncertainty is

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

the re-initiation of Bottom Water formation and enhancement of deep-water ventilation (Yoon et al., 2018). Projection of future acidification based on the past trend alone may prove to be erroneous. Another source of uncertainty in terms of the shoaling of the aragonite saturation horizon in the Ulleung Basin comes from the role of the intermediate water that forms in the western Japan Basin and flows south into the Ulleung Basin (Kim et al., 2004). While the aragonite saturation horizon in the Japan Basin shoaled from 350 m in 1999 to a depth a little shallower than 200 m in 2014, it did not change in the Ulleung Basin (Fig. 4 and Fig. S2). The intermediate water lies in the 200–400 m layer (Yoon and Kawamura, 2002), where the current aragonite saturation horizon is positioned. The strength of the intermediate water formation probably affects the saturation state of aragonite (Feely et al., 1984). Nonetheless, absorption of anthropogenic CO_2 will decrease the aragonite saturation state of the intermediate water.

5. Summary

Despite the similarity of the AOU and DIC levels in the ES to those in the South Atlantic, the ES carbonate chemistry resembles that of the North Pacific, where the DIC/TA ratio is high and the deep water is vulnerable to acidification. Carbonate saturation horizons are much shallower in the ES than in the South Atlantic. The large DIC supply caused by the high primary production and export in conjunction with low $CaCO_3$ export to the interior of the ES are responsible for the observed difference between the ES and the South Atlantic. The carbonate chemistry of the ES is similar to that in the eastern equatorial Pacific, where

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

upwelling-enhanced high primary productivity supplies large amounts of organic matter to the subsurface, which is already vulnerable to acidification because of the high DIC/TA ratio (Bates, 2018).

Acidification in the interior of the ES is occurring at a fast rate. The observed acidification in the ES has been caused mainly by the slowdown of ventilation and consequent accumulation of CO_2 from organic matter decomposition. However, the meridional gradients in AOU and DIC between the Japan and Ulleung basins, newly observed in 2014, indicate that the deep-water circulation is changing. The acidification trend may be reversed depending on the deep-water ventilation rate.

As suggested by Chen et al. (2017), ventilation slowdown in the oceans caused by global warming will acidify the deep layer (>1000 m), which is currently not experiencing significant anthropogenic CO_2 invasion. These authors also suggested that the ES provides an example of deep-water acidification caused by slowed ventilation (Chen et al., 2017). However, consideration should be given to the distinct characteristics of the carbonate chemistry of the ES. The ES is especially vulnerable to acidification and is likely to be a special case rather than a good example of how the deep Atlantic will respond to slowed ventilation.

Acknowledgements

We thank Guebuem Kim, SungHyun Nam, Doshik Hahm, and Yang-Ki Cho for discussion of the manuscript; Kyung-Ryul Kim and Kyung-Il Chang for their leadership in the earlier research of the East Sea; and Vyacheslav Lobanov for coordination of the Korea–Russia joint

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

research. We thank the captains and crews of R/V *Akademik Lavrentyev* and survey ship *Haeyang 2000* for their help at sea. This research forms part of the 'Deep Water Circulation and Material Cycling in the East Sea (20160040)' project funded by the Ministry of Oceans and Fisheries, Korea.

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

323 Bates, N. R.: Seawater Carbonate Chemistry Distributions Across the Eastern South Pacific
324 Ocean Sampled as Part of the GEOTRACES Project and Changes in Marine Carbonate
325 Chemistry Over the Past 20 Years, Front. Mar. Sci., 5, doi:10.3389/fmars.2018.00398,
326 2018.
327 Broecker, W. S. and Peng, T.-H.: Tracers in the Sea, Eldigio Press ed., Lamont Doherty
328 Geological observatory, Palisades NY, 690 pp., 1982.
329 Chen, C.-T. A., Wang, S.-L., and Bychkov, A. S.: Carbonate chemistry of the Sea of Japan, J.
330 Geophys. Res.-Oceans, 100, 13737-13745, doi:10.1029/95jc00939, 1995.
331 Chen, C.-T. A., Lui, H.-K., Hsieh, C.-H., Yanagi, T., Kosugi, N., Ishii, M., and Gong, G.-C.:
332 Deep oceans may acidify faster than anticipated due to global warming, Nat. Clim.
333 Change, 7, 890-894, doi:10.1038/s41558-017-0003-y, 2017.
334 Clayton, T. D., and Byrne, R. H.: Spectrophotometric seawater pH measurements: total
335 hydrogen ion concentration scale calibration of m-cresol purple and at-sea results, Deep-
336 Sea Res., 40, 2115-2129, 1993.
337 Dickson, A., and Millero, F. J.: A comparison of the equilibrium constants for the dissociation
338 of carbonic acid in seawater media, Deep-Sea Res. 34, 1733-1743, 1987.
339 Dickson, A. G., Sabine, C. L., and Christian, J. R. (Eds.): Guide to best practices for CO2
340 measurements, PICES Special Publication, 3, 191 pp., 2007.
341 Feely, R. A., Byrne, R. H., Betzer, P. R. Gendron, J. F., and Acker, J. G.: Factors influencing
342 the degree of saturation of the surface and intermediate waters of the North Pacific Ocean
343 with respect to aragonite, J. Geophys. Res., 89, 10631–10640,

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

344 doi:10.1029/JC089iC06p10631, 1984.
345 Feely, R. A., Sabine, C. L., Byrne, R. H., Millero, F. J., Dickson, A. G., Wanninkhof, R.,
346 Murata, A., Miller, L. A., and Greeley, D.: Decadal changes in the aragonite and calcite
347 saturation state of the Pacific Ocean, Global Biogeochem. Cy., 26, GB3001,
348 doi:10.1029/2011GB004157, 2012.
349 Hahm, D., and Kim, K.-R.: Observation of bottom water renewal and export production in
350 the Japan Basin, East Sea using tritium and helium isotopes, Ocean Sci. J., 43, 39-48,
351 2008.
352 Honjo, S., Manganini, S. J., Krishfield, R. A., and Francois, R.: Particulate organic carbon
353 fluxes to the ocean interior and factors controlling the biological pump: A synthesis of
354 global sediment trap programs since 1983, Prog. Oceanogr., 76, 217-285,
355 doi:10.1016/j.pocean.2007.11.003, 2008.
356 Joo, H., Park, J. W., Son, S., Noh, J.-H., Jeong, J.-Y., Kwak, J. H., Saux-Picart, S., Choi, J. H.,
357 Kang, C.-K., and Lee, S. H.: Long-term annual primary production in the Ulleung Basin
358 as a biological hot spot in the East/Japan Sea, J. Geophys. Res., 119, 3002-3011,
359 doi:10.1002/2014jc009862, 2014.
360 Joo, H., Son, S., Park, J.-W., Kang, J., Jeong, J.-Y., Lee, C., Kang, C.-K., and Lee, S.: Long-
361 Term Pattern of Primary Productivity in the East/Japan Sea Based on Ocean Color Data
362 Derived from MODIS-Aqua, Remote Sens., 8, doi:10.3390/rs8010025, 2015.
363 Joo, H., Son, S., Park, J. W., Kang, J. J., Jeong, J. Y., Kwon, J. I., Kang, C. K., and Lee, S. H.:
364 Small phytoplankton contribution to the total primary production in the highly productive

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

365 Ulleung Basin in the East/Japan Sea, Deep-Sea Res. Pt. II, 143, 54–61, 2017.
366 Kang, J. H., Kim, W. S., Chang, K. I., and Noh, J. H.: Distribution of plankton related to the
367 mesoscale physical structure within the surface mixed layer in the southwestern East Sea,
368 Korea, J. Plankton Res., 26, 1515-1528, 2004a.
369 Kang, D.-J., Kim, K., and Kim, K.-R.: The past, present and future of the East/Japan sea in
370 change: a simple moving-boundary box model approach, Prog. Oceanogr., 61, 175-191,
371 2004b.
372 Kawamura, H., and Wu, P.: Formation mechanism of Japan Sea Proper Water in the flux
373 center off Vladivostok, J. Geophys. Res., 103, 21611-21622, 1998.
374 Key, R. M.:: Ocean process tracers: Radiocarbon, edited by J. Steele, S. Thorpe, and K.
375 Turekian : in Encyclopedia of Ocean Sciences, Elsevier, NY., 2338-2353, 2001.
376 Key, R. M., Olsen, A., van Heuven, S., Lauvset, S. K., Velo, A., Lin, X., Schirnick, C., Kozyr,
377 A., Tanhua, T., and Hoppema, M.: Global Ocean Data Analysis Project, Version 2
378 (GLODAPv2). Carbon Dioxide Information Analysis Center, Oak Ridge Nat Lab, 2015.
379 Kim, J. Y., Kang, D. J., Lee, T., and Kim, K. R.: Long-term trend of CO2 and ocean
380 acidification in the surface water of the Ulleung Basin, the East/Japan Sea inferred from
381 the underway observational data, Biogeosciences, 11, doi:2443-2454, 10.5194/bg-11-
382 2443-2014, 2014.
383 Kim, K.-R., and Kim, K.: What is happening in the East Sea (Japan Sea)?: Recent chemical
384 observations during CREAMS 93-96, Ocean Sci. J., 31, 164-172, 1996.
385 Kim, K., Kim, K.-R., Min, D.-H., Volkov, Y., Yoon, J.-H., and Takematsu, M.: Warming and

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

structural changes in the east (Japan) Sea: A clue to future changes in global oceans?, Geophys. Res. Lett., 28, 3293-3296, doi:10.1029/2001gl013078, 2001.

Kim, K., Kim, K.-R., Kim, Y.-G., Cho, Y.-K., Kang, D.-J., Takematsu, M., and Volkov, Y.: Water masses and decadal variability in the East Sea (Sea of Japan), Prog. Oceanogr., 61, 157-174, 2004.

Kim, K. R., Kim, G., Kim, K., Lobanov, V., Ponomarev, V., and Salyuk, A.: A sudden bottom-water formation during the severe winter 2000–2001: The case of the East/Japan Sea, Geophys. Res. Lett., 29, 7571-7574, 2002.

Kim, M., Hwang, J., Rho, T., Lee, T., Kang, D.-J., Chang, K.-I., Noh, S., Joo, H., Kwak, J. H., Kang, C.-K., and Kim, K.-R.: Biogeochemical properties of sinking particles in the southwestern part of the East Sea (Japan Sea), J. Mar. Syst., 167, 33-42, doi:10.1016/j.jmarsys.2016.11.001, 2017.

Kumamoto, Y. i., Yoneda, M., Shibata, Y., Kume, H., Tanaka, A., Uehiro, T., Morita, M., and Shitashima, K.: Direct observation of the rapid turnover of the Japan Sea bottom water by means of AMS radiocarbon measurement, Geophys. Res. Lett., 25, 651-654, 1998.

Kwak, J. H., Hwang, J., Choy, E. J., Park, H. J., Kang, D.-J., Lee, T., Chang, K.-I., Kim, K.-R., and Kang, C.-K.: High primary productivity and f-ratio in summer in the Ulleung basin of the East/Japan Sea, Deep-Sea Res., 79, 74-85, doi:10.1016/j.dsr.2013.05.011, 2013a.

Kwak, J. H., Lee, S. H., Park, H. J., Choy, E. J., Jeong, H. D., Kim, K. R., and Kang, C. K.: Monthly measured primary and new productivities in the Ulleung Basin as a biological

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

"hot spot" in the East/Japan Sea, Biogeosciences, 10, 4405-4417, doi:10.5194/bg-10-4405-2013, 2013b.

Lee, K., Sabine, C. L., Tanhua, T., Kim, T.-W., Feely, R. A., and Kim, H.-C.: Roles of marginal seas in absorbing and storing fossil fuel CO 2, Energy Environ. Sci., 4, 1133-1146, 2011.

Lewis, E., Wallace, D., and Allison, L. J.: Program developed for CO2 system calculations, Brookhaven National Lab., Dept. of Applied Science, NY, 1998.

Mehrbach, C., Culberson, C., Hawley, J., and Pytkowicx, R.: Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure 1, Limnol. Oceanogr., 18, 897-907, 1973.

Olsen, A., Key, R. M., van Heuven, S., Lauvset, S. K., Velo, A., Lin, X., Schirnick, C., Kozyr, A., Tanhua, T., and Hoppema, M.: The Global Ocean Data Analysis Project version 2 (GLODAPv2)–an internally consistent data product for the world ocean, Earth Syst. Sci. Data, 8, 2016.

Otosaka, S., and Noriki, S.: Relationship between composition of settling particles and organic carbon flux in the western North Pacific and the Japan Sea, J. Oceanogr., 61, 25-40, 2005.

Park, G.-H., Lee, K., Tishchenko, P., Min, D.-H., Warner, M. J., Talley, L. D., Kang, D.-J., and Kim, K.-R.: Large accumulation of anthropogenic CO2in the East (Japan) Sea and its significant impact on carbonate chemistry, Global Biogeochem. Cycles, 20, doi:10.1029/2005gb002676, 2006.

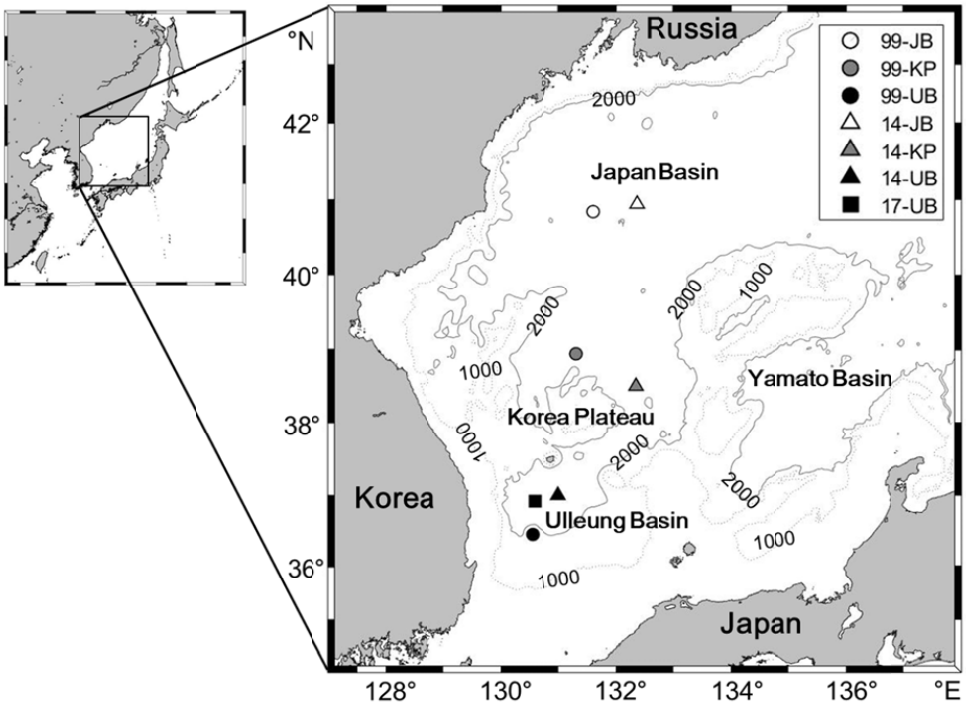
https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

428 Park, G.-H., Lee, K., and Tishchenko, P.: Sudden, considerable reduction in recent uptake of
429 anthropogenic CO2 by the East/Japan Sea, Geophys. Res. Lett., 35,
430 doi:10.1029/2008gl036118, 2008.
431 Senjyu, T., and Sudo, H.: Water characteristics and circulation of the upper portion of the
432 Japan Sea Proper Water, J. Mar. Syst., 4, 349-362, 1993.
433 Senjyu, T., Shin, H.-R., Yoon, J.-H., Nagano, Z., An, H.-S., Byun, S.-K., and Lee, C.-K.:
434 Deep flow field in the Japan/East Sea as deduced from direct current measurements,
435 Deep-Sea Res.earch Part II, 52, 1726-1741, 2005.
436 Sim, B.-R., Kang, D.-J., Park, Y. G., and Kim, K.-R.: Spatial and Temporal Variation of
437 Dissolved Inorganic Radiocarbon in the East Sea, Ocean Polar Res., 36, 111-119,
438 doi:10.4217/opr.2014.36.2.111, 2014.
439 Talley, L. D., Lobanov, V., Ponomarev, V., Salyuk, A., Tishchenko, P., Zhabin, I., and Riser,
440 S.: Deep convection and brine rejection in the Japan Sea, Geophys. Res. Lett. 30, 2003.
441 Talley, L. D., Tishchenko, P., Luchin, V., Nedashkovskiy, A., Sagalaev, S., Kang, D.-J.,
442 Warner, M., and Min, D.-H.: Atlas of Japan (East) Sea hydrographic properties in summer,
443 1999, Prog. Oceanogr., 61, 277-348, 2004.
444 Tsunogai, S., Watanabe, Y. W., Harada, K., Watanabe, S., Saito, S., and Nakajima, M.:
445 Dynamics of the Japan Sea deep water studied with chemical and radiochemical tracers,
446 in: Elsevier oceanography series, Elsevier, 105-119, 1993.
447 Yamada, K., Ishizaka, J., and Nagata, H.: Spatial and temporal variability of satellite primary
448 production in the Japan Sea from 1998 to 2002, J. Oceanogr., 61, 857-869, 2005.

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

449 Yoon, J.-H., and Kawamura, H.: The formation and circulation of the intermediate water in
450 the Japan Sea, J. Oceanogr., 58, 197-211, 2002.
451 Yoon, S. T., Chang, K. I., Nam, S., Rho, T., Kang, D. J., Lee, T., Park, K. A., Lobanov, V.,
452 Kaplunenko, D., Tishchenko, P., and Kim, K. R.: Re-initiation of bottom water formation
453 in the East Sea (Japan Sea) in a warming world, Sci Rep, 8, 1576, doi:10.1038/s41598-
454 018-19952-4, 2018.

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019



455

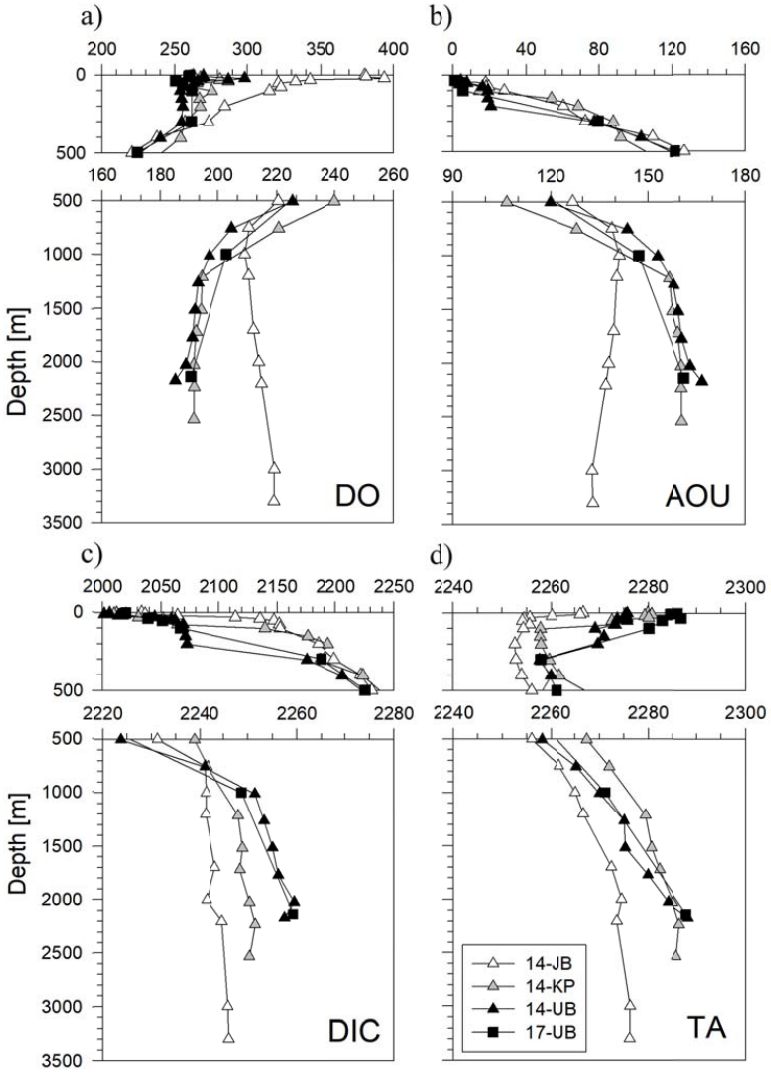
456 Figure 1. Bathymetric map of the East Sea (Japan Sea) showing study sites. Circles: 1999,

457 triangles: 2014, and a square: 2017.

458

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

Biogeosciences
Discussions
Open Access
EGU



459

460 Figure 2. Vertical distribution of a) dissolved oxygen, b) apparent oxygen utilization (AOU),
461 c) dissolved inorganic carbon, and d) total alkalinity (TA). All results are presented in µmol
462 kg^{-1}.

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

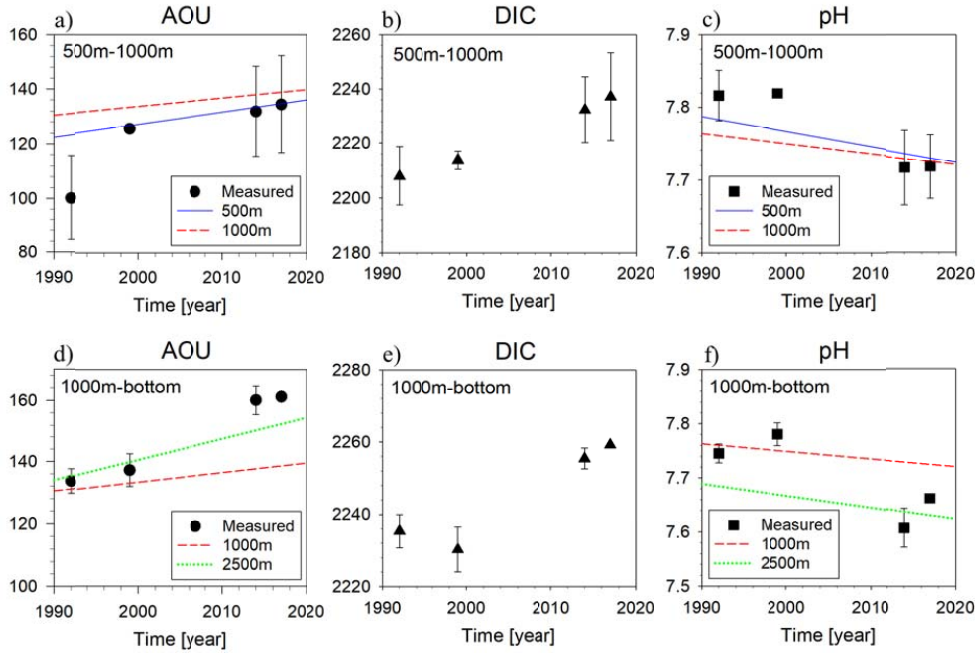


Figure 3. Temporal variations of AOU in μmol kg^{-1} (a, d), DIC (b, e) in μmol kg^{-1}, and pH on the total hydrogen scale (c, f) in the 500–1000 m layer (upper panels) and in the 1000 m to bottom layer (lower panels) in the Ulleung Basin. The mean and standard deviation in the corresponding layer are plotted. Temporal trends for AOU and pH presented in Chen et al. (2017) are also shown for comparison.

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

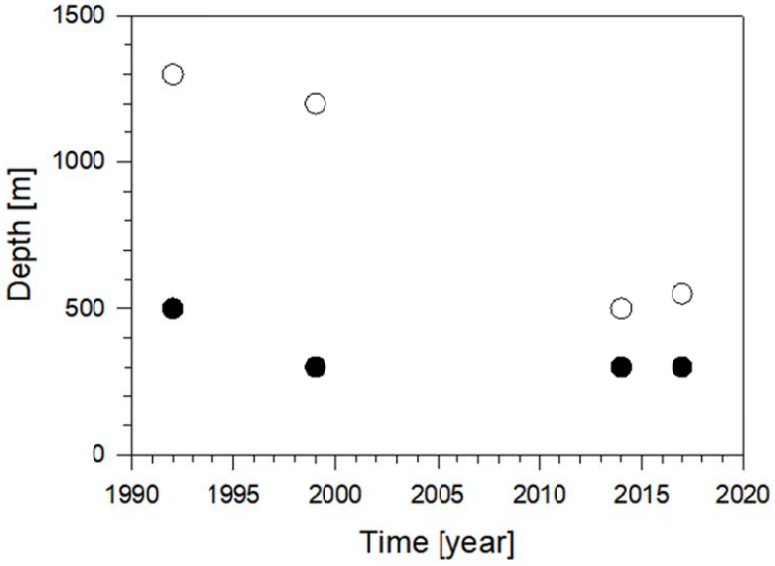


Figure 4. Temporal variations of calcite (open symbols) and aragonite (filled symbols) saturation horizons in the Ulleung Basin.

https://doi.org/10.5194/bg-2019-474
Preprint. Discussion started: 16 December 2019

Biogeosciences
Discussions
Open Access
EGU

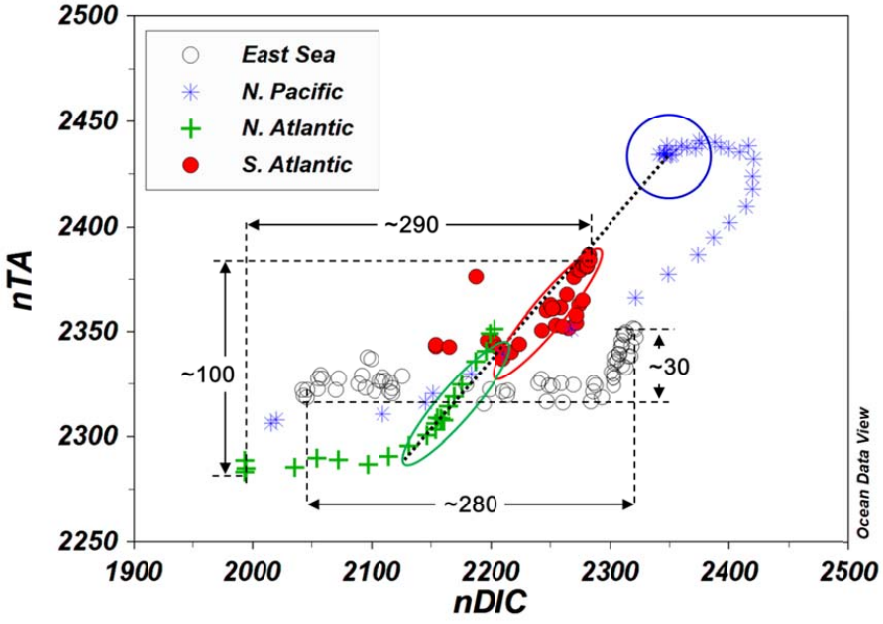


Figure 5. Plot of nTA against nDIC in the East Sea and at the three oceanic sites (vertical profiles are presented in Figure S3). A quasi-linear trend from the surface water of the North Atlantic to the deep water of the South Atlantic, and to the deep water of the North Pacific is apparent. The East Sea values show a distinct variation from that of the oceans. Approximate changes in nDIC and nTA from the surface water to the deep waters are indicated by the arrows.