Continental Shelf Research 111 (2015) 223–233

Contents lists available at ScienceDirect

Continental Shelf Research

journal homepage: www.elsevier.com/locate/csr

Research papers

Acidifying intermediate water accelerates the acidification of seawater on shelves: An example of the East China Sea

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ARTICLE INFO

Article history:
Received 1 April 2015
Received in revised form
1 August 2015
Accepted 17 August 2015
Available online 18 August 2015

Keywords:
Acidification
East China Sea
CO_2
pH
Upwelling
Ventilation

ABSTRACT

This study is the first to present observed acidification rates at the shelf break of the East China Sea (ECS) and in the Okinawa Trough between 1982 and 2007. The use of apparent oxygen utilization (AOU) data to quantify the change in pH due to physical changes and changes in biological activities is demonstrated. The results thus obtained reveal that the drop in pH of the Kuroshio Intermediate Water (KIW) in the ECS is a result of not only the intrusion of atmospheric CO_2, but also an increase in AOU concentration. The acidification rates caused by the increasing AOU concentration could contribute up to -0.00086 ± 0.00017 pH unit yr^{-1} at 900 m in the Okinawa Trough and -0.00082 ± 0.00057 pH unit yr^{-1} on the shelf break of the ECS. These values are equivalent to 54% and 51%, respectively, of the acidification rate of -0.0016 pH unit yr^{-1} based on an assumption of the air–sea CO_2 equilibrium. When the effects of changing AOU and θ are eliminated, the acidification rate in the basin of the ECS captures the rate of change that is caused by an increase in anthropogenic CO_2 concentration. In contrast, when the effects of changing AOU and θ are eliminated, the acidification rate at the shelf break is 69% higher than the rate based on an assumption of the air–sea CO_2 equilibrium. Since the seawater on the shelf contains a higher proportion of the South China Sea (SCS) seawater and coastal water than does that in the Okinawa Trough, the result herein may imply that the SCS seawater, coastal water, or a combination of them suffered a higher acidification rate during the studied period. This study, to the best of the authors' knowledge, is the first to demonstrate that changing the carbonate chemistry of both incoming offshore intermediate seawater and coastal water results in the acidification of seawater on a continental shelf. The results herein reveal a situation in which the acidification of coastal seawater may be faster than expected when the reduction of pH of the incoming offshore seawater is considered along with the increasing atmospheric CO_2 and terrestrial nutrient fluxes.

1. Introduction

Marine ecosystems, especially those on marginal seas, are affected by various human-induced stresses in the form of changes to their chemical and physical environments. Since the pre-industrial period, humans have released a massive amount of CO_2 to the atmosphere, largely by the burning of fossil fuels, and partly by the manufacturing of cement and deforestation. As major sinks of anthropogenic CO_2, the ocean and the land each absorbs about one-third of human-released CO_2. The rest remains in the atmosphere (Chen and Drake, 1986; Sabine et al., 2004a; Takahashi et al., 2009).

As a greenhouse gas, atmospheric CO_2 intensifies the greenhouse effect, warming the earth. The warming of seawater is a physical stressor for some species, such as coral. Additionally, an increase in the seawater temperature reduces the solubility of dissolved oxygen (DO) in seawater (Chen, 1981). Absorbed CO_2 dissolves in seawater to form carbonic acid, reducing the pH of the seawater and the saturation state of calcium carbonate (Ω). Reductions in pH, Ω, and DO content adversely influence marine living organisms.

Since the anthropogenic CO_2 concentration declines as depth increases (Chen and Millero, 1979; Ríos et al., 2010), the

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http://dx.doi.org/10.1016/j.csr.2015.08.014

acidification rate is expected to decrease with increasing depth. However, any change in respiration rate or seawater ventilation will also impact the vertical distribution of carbonate chemistry, and hence the acidification rate. Therefore, the acidification rate is not necessarily decreasing with increasing depth in all cases. The site of the European Station for Time Series Study (ESTOC), located in the northeast Atlantic Ocean, provides typical data that reveal that the rate of seawater acidification indeed decreases with increasing depth (Gonzalez-Davila et al., 2010). In the North Pacific Ocean, the subsurface seawater, and not the surface seawater, reportedly had the highest acidification rate between 1991 and 2006 (Byrne et al., 2010). Observations made at the Hawaii Ocean Time-Series (HOT) station are consistent with this finding that subsurface seawater has the highest acidification rates (Dore et al., 2009). This finding is suggested to arise from an ongoing slow-down in the ventilation of seawater in the North Pacific Ocean (Byrne et al., 2010). Therefore, more organic matter is decomposed, increasing the dissolved inorganic carbon (DIC) concentration, and the apparent oxygen utilization (AOU) concentration, but reducing pH and DO concentration.

In coastal regions, eutrophication accelerates the acidification of subsurface seawater. In recent decades, terrestrial nutrient fluxes have increased several times over their original values, causing the eutrophication of adjacent coasts. Therefore, hypoxia has spread widely (Diaz and Rosenberg, 2008). Additionally, the decomposition of the increased amount of organic matter on the bottom of the sea in the coastal regions, which results from eutrophication, consumes more DO and releases more CO_2, worsening the situation (Cai et al., 2011; Chen et al., 2008; Rabalais et al., 2010; Zhai et al., 2014). As a result, subsurface seawater in coastal regions suffers a large drop in pH on account of eutrophication.

In the East China Sea (ECS), the input of nitrate and phosphate from Changjiang (Yangtze River) has increased several times in recent decades (Wang, 2006) and eutrophication close to the mouth of Changjiang has become a serious problem (Chen et al., 2007; Wang, 2006). In the eastern region of the ECS, the Nagasaki Marine Observatory of the Japan Meteorological Agency (JMA) has regularly made oceanographic observations along the PN-Line (Fig. 1). Using the JMA data, recent studies have shown that concentrations of nutrients in the Kuroshio Intermediate Water (KIW) have also increased in the last two decades, but the DO concentration has fallen (Guo et al., 2012; Lui et al., 2014). The amounts of nutrients from both the land and the incoming seawater have increased, but the input of DO has decreased. Therefore, eutrophication and hypoxia may be becoming more severe throughout the ECS (Lui et al., 2014). However, changes in seawater carbonate chemistry in the ECS, based on observed long-term time series data, have not yet been reported.

Combining data from the PN-Line stations and from the stations of the Kuroshio-Edge Exchange Processes-Marginal Sea Study (KEEP-MASS) cruise that was conducted in the year 1992 (Fig. 1), this study will show for the first time the rate of temporal change of pH (dpH/dt) at various depths at the shelf-break and the deep basin of the ECS, called the Okinawa Trough. Physical and biological factors that may affect the acidification of seawater at the PN-Line are discussed. The use of AOU data to quantify the change in pH that is caused by a combination of changing biological activities (photosynthesis or respiration) and the vertical movement or mixing of seawater at various depths is demonstrated. Additionally, this study is one of the very few time-series

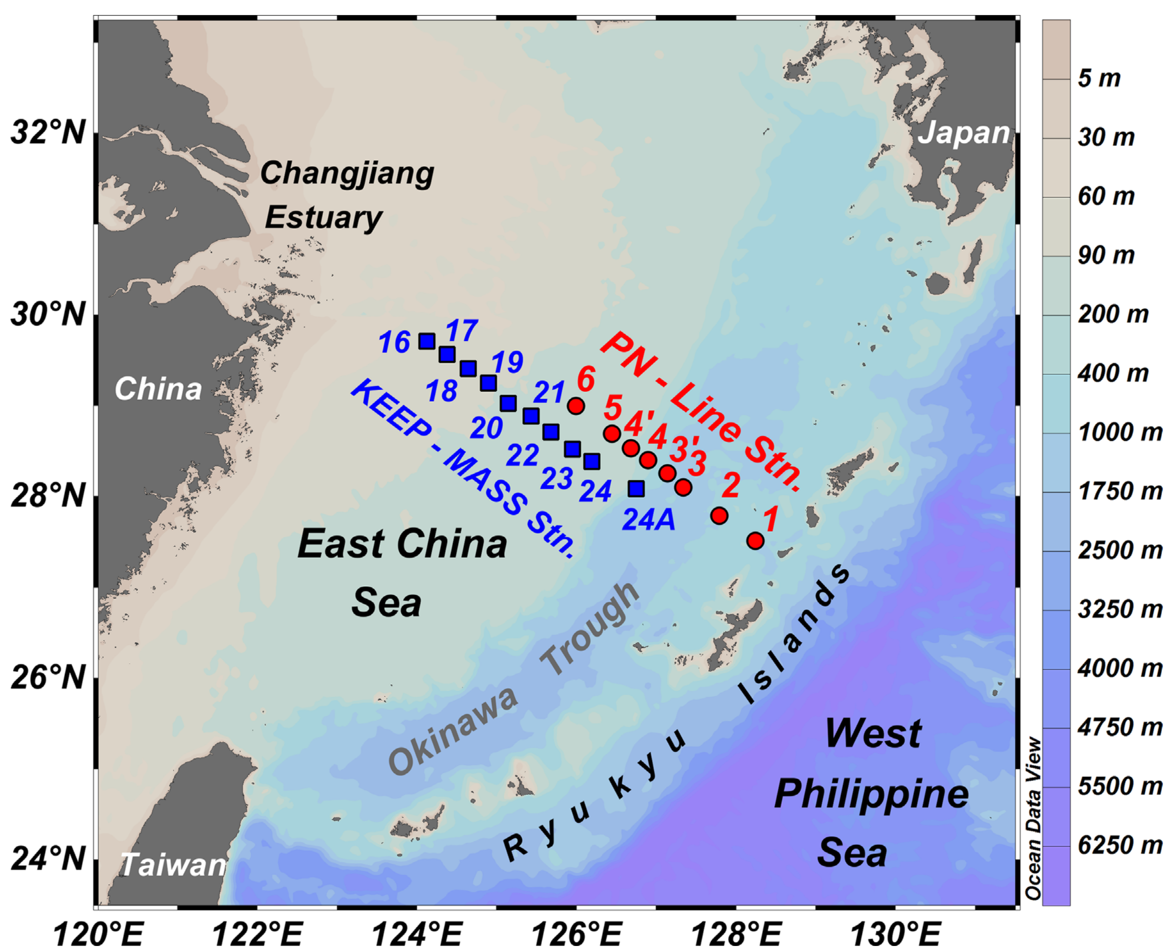

Fig. 1. Map of study area and stations.