Environmental Science

REVIEW

Roles of marginal seas in absorbing and storing fossil fuel CO$_2$

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We review data on the absorption of anthropogenic CO$_2$ by Northern Hemisphere marginal seas (Arctic Ocean, Mediterranean Sea, Sea of Okhotsk, and East/Japan Sea) and its transport to adjacent major basins, and consider the susceptibility to recent climatic change of key factors that influence CO$_2$ uptake by these marginal seas. Dynamic overturning circulation is a common feature of these seas, and this effectively absorbs anthropogenic CO$_2$ and transports it from the surface to the interior of the basins. Amongst these seas only the East/Japan Sea has no outflow of intermediate and deep water (containing anthropogenic CO$_2$) to an adjacent major basin; the others are known to be significant sources of intermediate and deep water to the open ocean. Consequently, only the East/Japan Sea retains all the anthropogenic CO$_2$ absorbed during the anthropocene. Investigations of the properties of the water column in these seas have revealed a consistent trend of waning water column ventilation over time, probably because of changes in local atmospheric forcing. This weakening ventilation has resulted in a decrease in transport of anthropogenic CO$_2$ from the surface to the interior of the basins, and to the adjacent open ocean. Ongoing measurements of anthropogenic CO$_2$, other gases and hydrographic parameters in these key marginal seas will provide information on changes in global oceanic CO$_2$ uptake associated with the predicted increasing atmospheric CO$_2$ and future global climate change. We also review the roles of other marginal seas with no active overturning circulation systems in absorbing and storing anthropogenic CO$_2$. The absence of overturning circulation enables anthropogenic CO$_2$ to penetrate only into shallow depths, resulting in less accumulation of anthropogenic CO$_2$ in these basins. As a consequence of their proximity to populated continents, these marginal seas are particularly vulnerable to human-induced perturbations. Maintaining observation programs will make it possible to assess the effects of human-induced changes on the capacity of these seas to uptake and store anthropogenic CO$_2$.

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1. Introduction

The global-scale burning of fossil fuels for energy over the past 250 years (the anthropocene) has largely contributed to the rapid increase in trace gas concentrations (including CO$_2$, CFCs, CH$_4$, N$_2$O, and other greenhouse gases) in the atmosphere.[1,2] These greenhouse gases influence the Earth's climate by trapping long-wave radiation, causing the Earth's surface to warm. During the

Broader context

An accurate assessment of the magnitude of future oceanic CO$_2$ uptake and storage is essential for guiding climate policies. A key scientific issue that is yet to be fully addressed is how oceanic uptake of anthropogenic CO$_2$ has evolved over time, and how variability in this process has been affected by recent trends in climate change. This critical issue can be better addressed in marginal seas, where the processes responsible for changing oceanic uptake of anthropogenic CO$_2$ are likely to change at much shorter time scales than the anthropocene. The four key marginal seas reviewed in this article—the Arctic Ocean, the Mediterranean Sea, the Sea of Okhotsk, and the East/Japan Sea—each stores proportionally more anthropogenic CO$_2$ than the global ocean. Dynamic overturning circulation is a common feature of these seas, and this effectively absorbs anthropogenic CO$_2$. Investigations of the properties of the water column in these seas have revealed a consistent trend of waning water column ventilation over time, probably because of changes in local atmospheric forcing. This weakening ventilation has resulted in a decrease in transport of anthropogenic CO$_2$ from the surface to the interior of the basins, and to the adjacent open ocean.

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anthropocene, only about half of the total CO_2 released by anthropogenic activities remains in the atmosphere; the remainder has been absorbed by the oceans and the land biosphere.[1]

The potential for storage of anthropogenic CO_2 in the global ocean is substantial because of the strong buffering capacity of seawater; the global ocean naturally contains approximately 50 times more carbon than the atmosphere.[3] When anthropogenic CO_2 is released into the atmosphere, the concentration gradient across the air–sea interface increases. This enhances the thermodynamic driving force for net CO_2 transfer from the atmosphere to the ocean in an effort to restore the concentration equilibrium. Therefore, surface water CO_2 concentrations over broad oceanic regions increase at similar rates to the atmospheric CO_2 concentration.[4] Most, but not all of the CO_2 absorbed by the ocean reacts with seawater to form carbonic acid (H_2CO_3), much of which dissociates releasing hydrogen ion (H^+), bicarbonate (HCO_3^-) and, to a lesser extent, carbonate (CO_3^{2-}) ions into the seawater (Fig. 1). For typical surface ocean conditions, approximately 90% of the total dissolved inorganic carbon ($C_T = [CO_2aq] + [HCO_3^-] + [CO_3^{2-}]$) is in the form of HCO_3^-, 9% occurs as CO_3^{2-}, and only 1% remains as undissociated CO_2 and H_2CO_3, $[CO_2aq]$ (Fig. 1). Here we define the term anthropogenic CO_2 as the increase in C_T that has resulted from rising concentrations of CO_2 in the atmosphere. Thus anthropogenic CO_2 only enters the ocean through air–sea exchange. Changes in the oceanic carbon pool because of changes in lateral input and biological or remineralization activities are not considered here.

Although the ocean is capable of storing a considerable amount of anthropogenic CO_2, the future evolution of this

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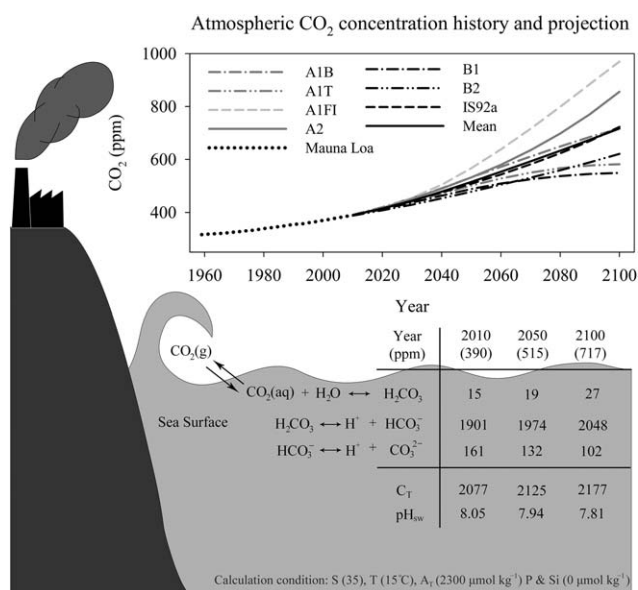
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Fig. 1 History of atmospheric CO_2 concentration at Mauna Loa from 1958 to 2009 (dotted line; downloaded from ftp://ftp.cmdl.noaa.gov/ccg/co2/trends/co2_mm_mlo.txt), and projections (other lines) and changes in ocean carbonate chemistry in response to atmospheric CO_2 concentration change under IPCC emission scenarios.[2] The table (lower right corner) shows the expected values of carbon parameters (H_2CO_3, HCO_3^-, CO_3^{2-}, C_T and pH) in the seawater equilibrium, and the mean atmospheric CO_2 concentrations (in parentheses) for three selected years (2010, 2050 and 2100). Values of carbon parameters in the table were calculated at $S = 35$ and temperature = 15 °C for $A_T = 2300$ μmol kg^{-1} and pCO$_2$ = 390, 515, or 717 using the carbonic acid dissociation constants of *Mehrbach et al.*,[124] as refitted by *Dickson and Millero*.[125]

critical sink is unclear because of uncertainties in projections of climatic change. An accurate assessment of the magnitude of future oceanic CO_2 uptake and storage is essential for guiding climate policies. The major conclusion from analyses of the global carbon data (obtained from surveys in the 1990s) is that as of 1994 the global ocean has stored approximately 48% of the total CO_2 emissions from fossil fuel burning and cement production during the anthropocene.[5] A key scientific issue that is yet to be fully addressed is how oceanic uptake of anthropogenic CO_2 has evolved over time, and how variability in this process has been affected by recent trends in climate change.[6,7] This critical issue can be better addressed in marginal seas, where the processes responsible for changing oceanic uptake of anthropogenic CO_2 are likely to change at much shorter time scales than the anthropocene.

Unlike the major ocean basins, the role of marginal seas as a sink of atmospheric CO_2 has been understudied because of a traditional belief that their small surface area (only 7% of the world's ocean area) indicates a minor role in absorbing and storing anthropogenic CO_2. However, marginal seas typically have enormous potential for the absorption of anthropogenic CO_2 from the atmosphere,[8] as utilization of high nutrient inputs from adjacent lands can reduce the surface water CO_2 concentration and the direct interaction between the resulting organic matter deposited onto the sediments and overlying seawater can generate alkalinity,[9] both of which drive CO_2 transfer from the atmosphere to the ocean. In particular, marginal seas, where overturning circulation occurs on decadal to century time scales, are a critical yet underappreciated component of the ocean carbon sink.

There have been several extensive reviews of the current knowledge of biogeochemical processes occurring in global marginal seas,[10–14] but few have emphasized the amount of anthropogenic CO_2 stored or the mechanisms that underlie uptake and subsequent transfer of CO_2 to the interior water column, and potentially to the open ocean. Marginal seas including the Arctic Ocean,[15,16] the Mediterranean Sea,[17,18] the Sea of Okhotsk[19,20] and the East/Japan Sea[7,21] have been the subject of recent studies (Table 1). These basins are fully ventilated at all depths within timescales significantly shorter than the period of anthropogenic increase in atmospheric CO_2. The ventilated processes include

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Table 1 Anthropogenic CO_2 (C_{ant}) inventories or net CO_2 air-sea fluxes in the selected marginal seas

	Surface area/10^{12} m^2	Water volume/10^{15} m^3	Total C_{ant} inventory/Pg C	Specific C_{ant} inventory[a]/mol C m^{-2}	Reference year[b]	Transport to major basins/Pg C y^{-1}
Arctic Ocean	14	18	2.5–3.3[16]	15–20	2005	0.036 ± 0.005[42] (North Atlantic)
Mediterranean Sea	2.5	3.8	1.7 ± 0.4[18]	57 ± 13	2001	0.03 ± 0.003,[17] 0.025 ± 0.0006,[66]
Okhotsk Sea	1.6	1.4	0.18 ± 0.08[78]	9.4 ± 4.2	1980	0.032–0.066,[67] (North Atlantic) 0.025,[73] 0.006,[74] 0.011–0.18,[10] (North Pacific)
East/Japan Sea	0.98	1.7	0.40 ± 0.06[6]	34 ± 5.1	1999	~0[6] (North Pacific)
East China Sea	1.3	0.40	0.07 ± 0.02[10]	4.7 ± 1.3	1992	Na[c]
South China Sea	3.5	3.7	0.43 ± 0.10,[10] 0.60 ± 0.15[95]	10 ± 2.3,[10] 14 ± 3.5,[95] 16.6[96]	1994,[10] 1990s,[95] 1999–2003[96]	Na
Bering Sea	2.3	3.5	0.21 ± 0.05[10]	7.7 ± 1.8	1980	Na
Net air-sea flux[d]/ mol C m^{-2} y^{-1}						
North Sea	0.58	0.042	1.38[100]		2001–2002	0.008[100]
Red Sea	0.44	0.23	−0.23,[105] −0.91[107]		1977–1982	Na
Black Sea	0.44	0.55	7.3[13,110]		1988	Na
Gulf of Mexico	1.6	2.45	−1.70[112]		Na	Na

[a] Specific C_{ant} inventory for an individual basin was calculated by dividing the total C_{ant} inventory by its surface area. [b] A year for which either C_{ant} inventory or CO_2 uptake rate was estimated. [c] "Na" indicates not available. [d] Positive and negative values indicate air-to-sea and sea-to-air fluxes, respectively.

subduction, open ocean convection, and brine rejection during sea ice production.[22–25] Regional and global climate changes can affect these processes, and have profound impacts on ventilation and abyssal water properties, including the transfer efficiency of dense surface water loaded with anthropogenic CO_2 to the interior of the basins.[26] These basins have undergone significant changes in overturning circulation over the past 50 years, and consequently the properties of associated intermediate and deep waters have been affected.[27–31] Here we review recent key findings that are critical in assessing the uptake and transport of anthropogenic CO_2 in these actively ventilated marginal seas. We also consider other marginal seas that may be important in storing and transporting anthropogenic CO_2, including the East and South China Seas, the Bering Sea, the North Sea, the Red Sea, the Black Sea, and the Gulf of Mexico (Table 1).

2. Methods used to determine oceanic anthropogenic CO_2 content

Anthropogenic CO_2 data presented in this paper were estimated using one of the following three methods: the ΔC^* method, the transit time distribution (TTD) method, and the tracer combining O_2, C_T, and alkalinity (A_T) (TrOCA) method. In this section, we briefly describe the basic concepts of these methods. More detailed descriptions can be found elsewhere.[3,32–40] All three methods are based on observations and assume that anthropogenic CO_2 penetrates the ocean interior as a passive tracer in response to an evolving history in surface waters.

The ΔC^* method[32,33] is based on the premise that anthropogenic CO_2 (C_{ant}) can be separated out from measured C_T (C_T^{MEAS}) by subtracting the contribution from organic matter oxidation and $CaCO_3$ dissolution (ΔC^{BIO}), the C_T (C_T^{EQ}) that would be in equilibrium with a preindustrial atmospheric CO_2 of 280 μatm, and the C_T (C^{DISEQ}) arising from disequilibrium of the fugacity of CO_2 between the atmosphere and ocean using the equation $C_{ant} = C_T^{MEAS} - \Delta C^{BIO} - C_T^{EQ} - C^{DISEQ}$. Among the three subtracted terms in this equation, C_T^{EQ} is the largest, followed by ΔC^{BIO} and then C^{DISEQ}.

The transit time distribution (TTD) method[35–37] uses the fact that anthropogenic CO_2 in the ocean interior at a given time should be related to the concentration history of anthropogenic CO_2 at the surface and the distribution of times required for the water to reach to the present location within the ocean interior. The transit time distributions are approximated by inverse Gaussian functions based on transient tracer data (*e.g.*, CFCs).

The TrOCA method,[38–40] defined as TrOCA = O_2 + [C_T − 0.5A_T]/[C/O + 0.5N/O], estimates anthropogenic CO_2 in seawater from the difference between the measured TrOCA conservative tracer and a performed TrOCA tracer. However, this method has been shown to be associated with significant biases in a study comparing observations and model output.[41]

3. Marginal seas with overturning circulation systems

3.1. The Arctic Ocean

The Arctic Ocean is connected to the North Pacific Ocean by the Bering Strait and to the North Atlantic Ocean *via* exchange over
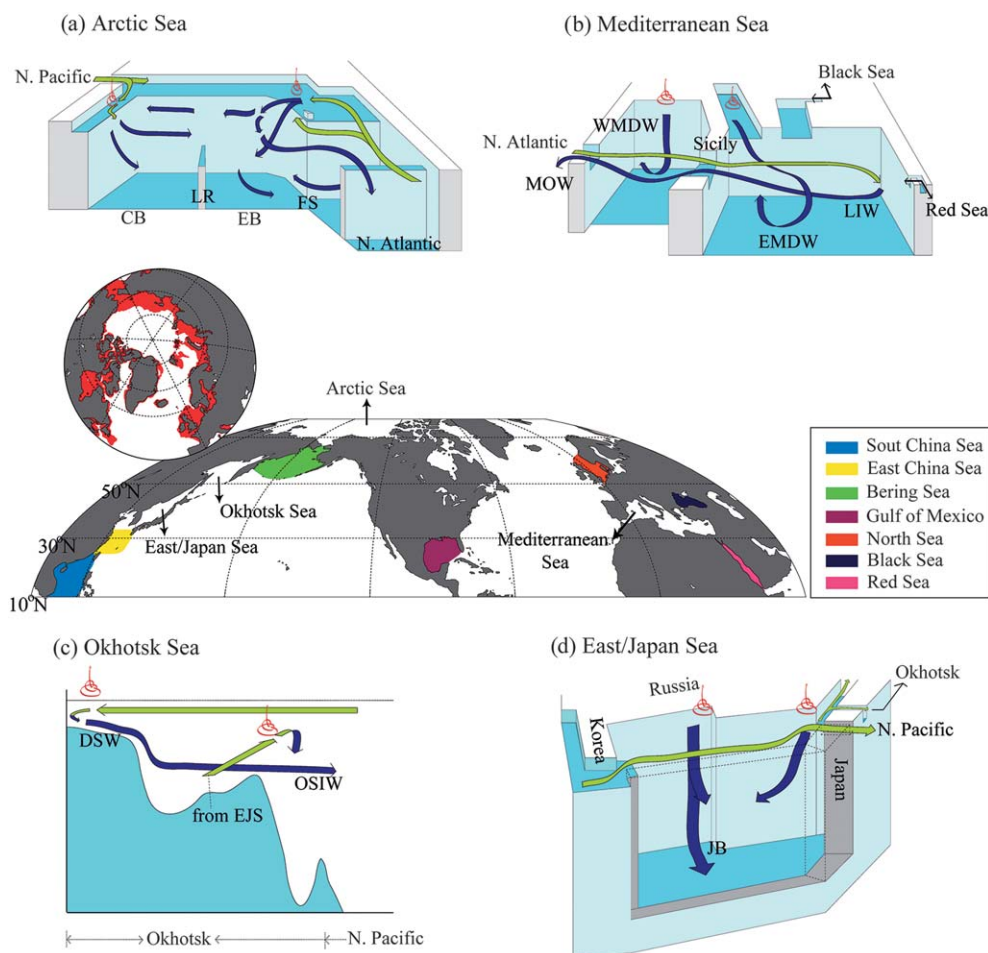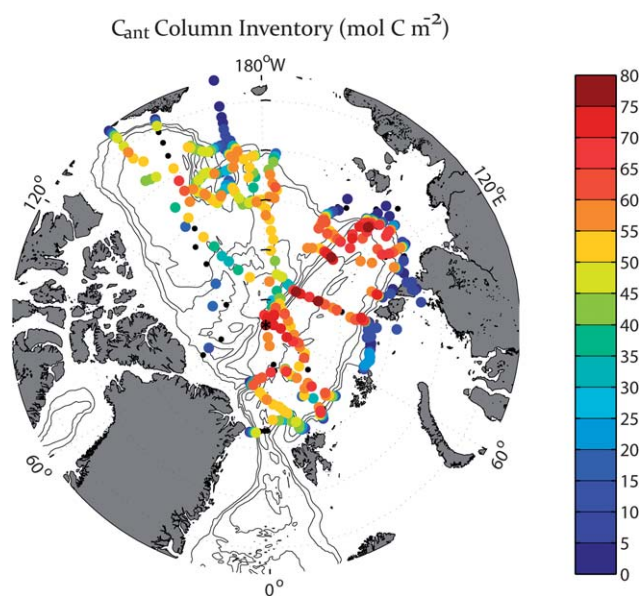
Fig. 2 Circulation patterns in (a) the Arctic Ocean, (b) the Mediterranean Sea, (c) the Sea of Okhotsk and (d) the East/Japan Sea. The red shading in (a) indicates the shelf regions (<200 m). The colored shadings represent the seven marginal seas discussed in Section 4. The green and blue lines (with arrows) indicate surface and deep (or intermediate) water flows, respectively. The red curls indicate heat loss due to either cooling or wind. LR, Lomonosov Ridge; CB, Canadian Basin; EB, Eurasian Basin; FS, Fram Strait; DSW, Dense Shelf Water; MOW, Mediterranean Overflow Water; LIW, Levantine Intermediate Water; EMDW, Eastern Mediterranean Deep Water; WMDW, Western Mediterranean Deep Water; OSIW, Okhotsk Sea Intermediate Water; EJS, East/Japan Sea; JB, Japan Basin.

the Greenland–Scotland Ridge system, over which dense water flows to the North Atlantic Ocean (Fig. 2a). These connections provide a direct link between changing conditions in the Arctic Ocean and the global ocean. Some of the anthropogenic CO_2 in the Arctic Ocean is absorbed directly from the overlying atmosphere, but much of it is absorbed elsewhere and transported to the Arctic in the Atlantic Ocean water entering the Arctic Ocean.[16] Within the Arctic Ocean the highest concentrations of anthropogenic CO_2 are found in the Atlantic Water layer north of the European shelf;[16] Arctic bottom waters also contain detectable levels of anthropogenic CO_2 (up to 8 µmol kg^{-1}).[16] Discernable differences in the concentration of anthropogenic CO_2 are found across the deep basins of the Arctic Ocean, with higher concentrations in the Eurasian Basin than in the Canadian Basin.[15,16] This mainly reflects differences in the mean age of deep water and the buffering capacity of seawater. Active ventilation of intermediate water in the Arctic Ocean transports a considerable amount of anthropogenic CO_2 to the interior of the Arctic Ocean. The anthropogenic CO_2 inventory for the Arctic Ocean as of 2005 has been calculated to be 2.5–3.3 Pg C,

based on transient tracer distributions.[16] This value is approximately 2% of the global inventory of anthropogenic CO_2 (142 ± 23 Pg C, referenced to the same year), even though the Arctic Ocean comprises only about 1% of the global ocean volume (Fig. 3). A significant amount of anthropogenic CO_2 (~0.036 Pg C y^{-1}) is transported from the Arctic Ocean and the Nordic seas through the Denmark Strait to the North Atlantic Ocean,[42] where the North Atlantic Deep Water is formed. Recent studies have indicated that the water from the Arctic Ocean becomes an increasingly important component of the North Atlantic Deep Water.[43,44] As Atlantic Ocean water entering the Arctic Ocean through the Nordic seas is a major source of anthropogenic CO_2 for the Arctic Ocean, a reported decline in anthropogenic CO_2 uptake by the subpolar North Atlantic Ocean in the last decade could affect the anthropogenic CO_2 budget for the Arctic Ocean.[45,46]

Existing data do not provide sufficient information to clarify how the Arctic Ocean has evolved as a reservoir of anthropogenic CO_2 or how the transport of anthropogenic CO_2 from the Arctic Ocean to the North Atlantic Ocean has changed over time. Several likely scenarios, based on our current understanding of

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Fig. 3 Water column inventory of anthropogenic CO_2 (C_{ant}) per unit area (mol C m^{-2}) in the Arctic Ocean, as of 2005. Anthropogenic CO_2 was determined using the transient tracer distribution method based on CFC-12, CFC-11 and SF_6 data (see ref. 16 for more details). Only stations with sufficient tracer data to enable water column inventory calculations are shown. Depth contours indicate 1000 m intervals. Redrawn using the same data used in ref. 16.

the Arctic Ocean, are worthy of consideration, as they will bring focus on uncertainties including how changes in the observed physical framework of the Arctic Ocean will affect the uptake of anthropogenic CO_2 from the atmosphere, and its storage in the interior. Satellite and other observations show that the Arctic Ocean ice cover is retreating more rapidly than recent models have predicted.[47] River discharge to the Arctic Ocean increased, on average, annually by 2.0 km^3 y^{-1} during the period 1936–1999, and 5.6 km^3 y^{-1} during the period 1964–2000.[48,49] The increased melting of sea ice and river discharges is contributing to making the Arctic Ocean surface waters less saline, although the A_T values of these two fresh water sources are different. Most of the Arctic Ocean surface water is currently undersaturated with respect to atmospheric CO_2, particularly under the sea ice, which restricts air–sea exchange of CO_2.[50–53] The loss of sea ice in summer will stimulate the CO_2 drawdown to the presently undersaturated mixed layer, simply by exposing more open water to air–sea exchange processes. Assuming full saturation in the mixed layer, the potential CO_2 uptake is estimated to be 48 and 7 g C m^{-2} for the Eurasian Basin and the Makarov Shelf slope, respectively.[50] Using these estimates, *Anderson and Kaltin*[50] calculated the potential CO_2 uptake of the entire deep central Arctic Ocean to be 0.28 Pg C. This uptake would be a one-time event. Extrapolation of results from the highly undersaturated Chukchi Sea to the Arctic Ocean indicates that the one-time uptake capacity of the entire Arctic mixed layer is 1.2 Pg C.[52] In addition, *Bates et al.*[52] calculated that the Arctic Ocean CO_2 sink has increased from 0.024 Pg C y^{-1} in the early 1970s to 0.066 Pg C y^{-1} in the early 2000s as a result of decreasing sea ice cover.

Enhanced summer melting of sea ice will decrease the salinity of the surface mixed layer, which will increase the solubility of

CO_2 and thereby the sink of CO_2. The increase in the sink because of declining salinity has been estimated to be 0.014 Pg C.[50] It is also anticipated that more storms will occur in the Arctic Ocean as global warming increases.[54,55] As the air–sea CO_2 exchange is markedly influenced by wind speed and the mixed layer often remains undersaturated throughout the year, stronger winds could further govern the uptake of CO_2 by the Arctic Ocean.[54,56]

3.2. The Mediterranean Sea

The Mediterranean Sea is a semi-enclosed basin with narrow connections to the Atlantic Ocean (through the Strait of Gibraltar) and the landlocked Black Sea (through the Bosphorus Strait). It also has an artificial connection to the Red Sea through the Suez Canal. Two principal overturning circulation cells play a critical role in transporting anthropogenic CO_2 from the Mediterranean Sea surface to the interior, and subsequently to the intermediate layer of the Atlantic Ocean (Fig. 2b). The major pattern is the formation of Mediterranean Intermediate Water. The Atlantic surface water entering the Mediterranean Sea progressively increases in salinity (up to 10%) through evaporation as it moves eastward. This salty water sinks in the eastern basin and becomes the Levantine Intermediate Water (LIW).[57] The LIW then flows westward (in the opposite direction to the surface water flow), and eventually flows into the Atlantic Ocean as intermediate water.[58] A secondary pattern involves the transformation of surface and intermediate water into either Western Mediterranean Deep Water (WMDW) or Eastern Mediterranean Deep Water (EMDW). In the western Mediterranean basin the persistent cold, dry winds that blow from the north in winter increase the salinity of the surface water.[23] These two deep water masses are denser than the LIW, and direct mixing between the EMDW and the WMDW is prevented by the
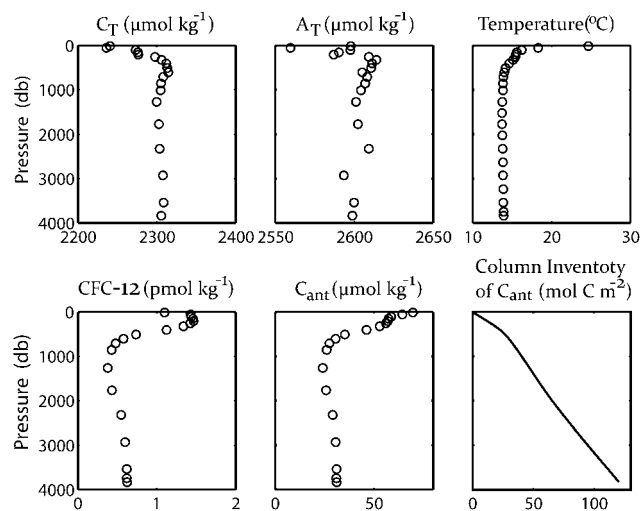
Fig. 4 Profiles of C_T, A_T, temperature, CFC-12 concentration, anthropogenic CO_2 (C_{ant}), and the cumulative column inventory of C_{ant}, obtained from a station (34.50°N, 19.00°E) in the Mediterranean Sea. The data used in these profiles were collected in 2001 on the R/V Meteor (cruise 51/2). The concentration of C_{ant} was calculated using the Transient Tracer Distribution method based on CFC-12 data (see ref. 18 for more details).

(a) C_{ant} Column Inventory (mol C m^{-2})

(b) C_{ant} (μmol kg^{-1})
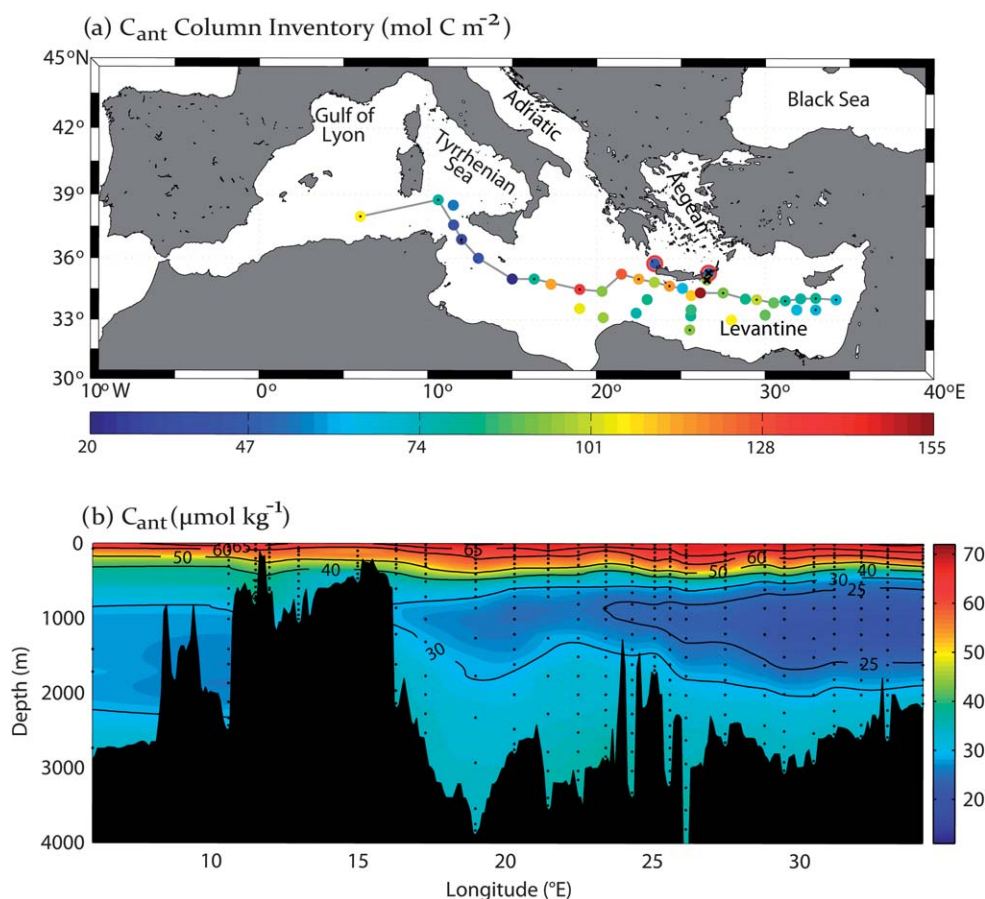
Fig. 5 (a) Stations on the R/V Meteor 51/2 cruise in 2001 and the water column anthropogenic CO_2 (C_{ant}) inventory per unit area (mol C m^{-2}) in the Eastern Mediterranean Sea. (b) Anthropogenic CO_2 (μmol kg^{-1}) in the section encompassed by the gray line in (a), calculated using the transient tracer distribution method based on CFC-12 data. Redrawn using data provided by the lead author of ref. 18 (see ref. 18 for more details).

presence of the Strait of Sicily. During recent decades, significant changes in the circulation and ventilation of the Mediterranean Sea have been observed.[28,59] Some of these changes seem to be part of a decadal oscillation pattern that causes deep water formation to alternately occur in the Aegean and Adriatic.[60]

Seawater carbon data for the Mediterranean Sea are scarce. *Schneider et al.*[18] suggested that high A_T surface water near the northern coast is transported to the interior of the basin as a consequence of deep water formation. High surface A_T values largely result from the influence of river discharges and the Black Sea inflow, both of which are high in A_T. Based on analysis of C_T and A_T data from the basin interior, *Schneider et al.*[18] further suggested that when it had last contact with the atmosphere the newly formed deep water was probably undersaturated with respect to the atmospheric pCO_2 value. This is supported by direct observations of undersaturated surface water pCO_2 in late winter (the time of deep water formation) in the northwestern Mediterranean Sea (43°25′N, 7°52′E; the DYFAMED time-series).[61] Analysis using transient tracer data indicates that anthropogenic CO_2 occurs throughout the entire water column of the Mediterranean Sea, with the maximum column inventory being ~150 mol m^{-2} (Fig. 4 and 5); the total basin-wide inventory was estimated to be 1.7 Pg C (range 1.3–2.1 Pg C) as of 2001.[18] The water column inventory of anthropogenic CO_2 for the Mediterranean Sea is considerably higher than that for the

Atlantic Ocean (66–72 mol C m^{-2})[62] and the Pacific Ocean (20–30 mol C m^{-2})[63] in the same latitude band, and higher even than the actively ventilating East/Japan Sea (~80 mol C m^{-2}).[6] Estimates of the anthropogenic CO_2 content of the water column, made using the TrOCA,[64] were higher than those determined using the transient tracer method.[18] The data of *Rivaro et al.*[64] imply an increase in pCO_2 of up to 200 μatm in surface waters during the anthropocene, which is approximately twice the pCO_2 increase observed in the atmosphere during the same period. The TrOCA method was also applied to decade-long measurements (1993–2005) of hydrographic and carbon parameters in the northwestern Mediterranean Sea (the DYFAMED time-series).[65] The resulting calculations indicated a decreasing concentration of anthropogenic CO_2, despite a significant increase in the C_T concentration in all layers in response to an increase in the atmospheric CO_2 during the study period.[65] Although the two methods (transient tracer *versus* TrOCA) do not yield consistent results, they point to a high water column inventory of anthropogenic CO_2 in the Mediterranean Sea. This is directly associated with active overturning circulation and the high A_T and temperature throughout the water column (Fig. 4); these are the dominant factors determining the uptake of anthropogenic CO_2 in the Mediterranean Sea.

A further important factor influencing the anthropogenic CO_2 content of the Mediterranean Sea is the exchange of seawater

between the Atlantic Ocean and the Mediterranean Sea across the Strait of Gibraltar. The inflow to the Mediterranean Sea is generally greater than the intermediate outflow to the Atlantic Ocean, whereas there is a net outflow of C_T (the sum of the naturally occurring and anthropogenic components) to the Atlantic Ocean because intermediate outflow contains higher C_T concentration than the surface inflow.[66] This exchange of seawater also influences the anthropogenic CO_2 content of the Mediterranean Sea; the outflow from the Mediterranean Sea to the intermediate layers of the Atlantic Ocean transports the anthropogenic CO_2 at a rate of 0.03–0.066 Pg C y^{-1}, and is thus a significant source of anthropogenic CO_2 to the Atlantic Ocean.[17,66,67] However, there is a net inflow of anthropogenic CO_2 to the Mediterranean Sea through the Strait of Gibraltar, as the inflowing surface layer contains more anthropogenic CO_2 than the outflowing intermediate water. Assessment of the magnitude of net inflow of anthropogenic CO_2 to the Mediterranean Sea is subject to uncertainties because the anthropogenic CO_2 concentration in the outflowing intermediate water inferred using the TrOCA method[67] generally yields anthropogenic CO_2 concentrations significantly higher than those determined using the other methods.

The intensity of overturning circulation in the Mediterranean Sea is subject to change, possibly due to global and local climate perturbations. Extensive hydrographic data for the western Mediterranean Sea over the past 50 years have shown an increase in the mean potential temperature of deep water (>2000 m), although interannual variations are considerable.[27,68] These deep water records reflect the average evolution of climate conditions at the surface during winter, when the deep water is formed. Together with other information (the heat budget and water flux), this trend of warming of deep water in the Mediterranean Sea suggests that greenhouse gas-induced local warming may be involved.[27,69]
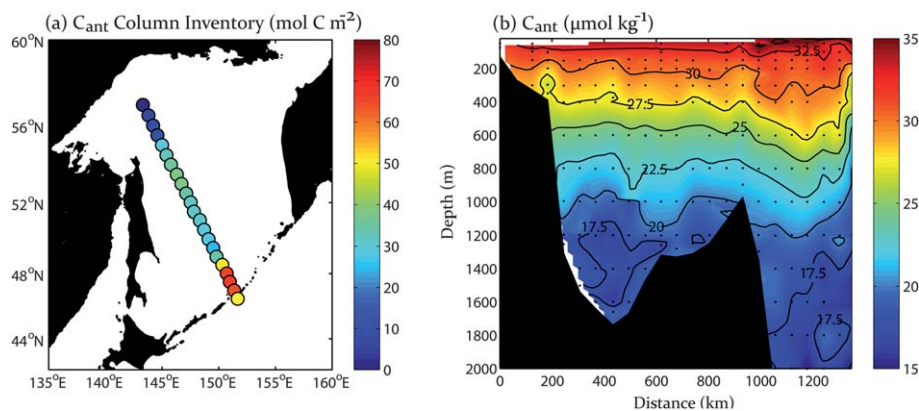
3.3. The Sea of Okhotsk

The Sea of Okhotsk is enclosed by land on three sides but is open to the North Pacific Ocean to the southeast. Shelves in the Sea of Okhotsk account for approximately 40% of the surface area.[10] This sea is the southernmost sea ice region in the Northern

Hemisphere and a source of North Pacific Intermediate Water (NPIW),[70] which is the densest water produced in the North Pacific Ocean. In the northwestern shelf region the dense water produced during sea ice formation sinks and contributes approximately 70% of the Okhotsk Sea Intermediate Water (OSIW),[71,72] which subsequently flows into the intermediate layer of the NPIW (Fig. 2c).[24,70] Therefore, the formation of dense shelf water during sea ice formation is a crucial process influencing the formation of OSIW and NPIW.

Direct observations using the ΔC^* method[32] indicate that the anthropogenic CO_2 has penetrated into the bottom (as deep as 1700 m) of the basin, where its concentration in near bottom waters reaches 15–20 μmol kg^{-1} (Fig. 6). The formation of cold
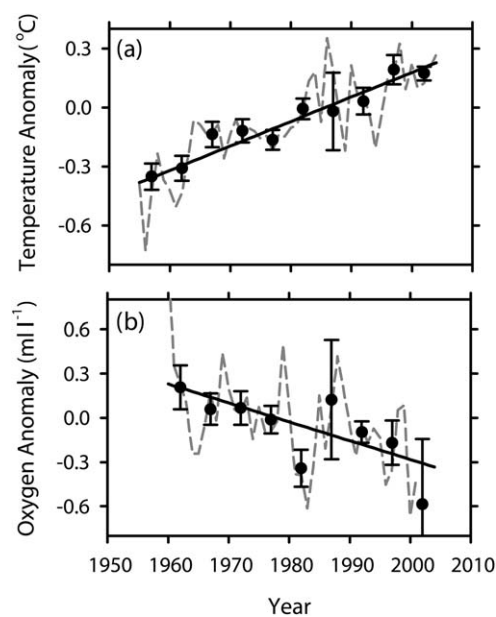
Fig. 7 Time series data (dashed gray lines) of (a) potential temperature anomalies and (b) dissolved oxygen anomalies (ml l^{-1}) at $27.0\sigma_\theta$ averaged over the Sea of Okhotsk. Filled circles indicate 5-year mean anomalies, with errors at the 95% confidence interval. Solid lines indicate linear regressions for the data of each time series. Redrawn using data provided by the lead author of ref. 30.

Fig. 6 (a) Water column anthropogenic CO_2 (C_{ant}) inventory per unit area (mol C m^{-2}) at the sampling locations, as of 1993. Black dots indicate the sampling depths. (b) Meridian section of anthropogenic CO_2 (μmol kg^{-1}) in the Sea of Okhotsk (calculated using the ΔC^* method[32] based on CFCs and carbon data collected during the World Ocean Circulation Experiment P1W).

and dense water (approximately 1 Sv, 10^6 m^3 s^{-1})[73] on the continental shelf affects not only the absorption of anthropogenic CO_2 but also its transport to the interior of the Sea of Okhotsk.[19,20] Strong winds in conjunction with intense vertical mixing in winter could enhance the uptake of anthropogenic CO_2 and its penetration into the intermediate layer. The anthropogenic CO_2 transported to the intermediate layers amounts to 10–30 g C m^{-2} y^{-1},[10,19,20] resulting in an anthropogenic CO_2 of 25–30 μmol kg^{-1} in the intermediate layers[74] (i.e. 27.05 σ_θ density surface or ∼600 m; Fig. 6b). This is 2–6 times greater than the mean uptake rate of anthropogenic CO_2 per unit area by the global ocean.[75] The sinking of dense shelf water to intermediate depths has also increased the concentration of anthropogenic CO_2 and other anthropogenic tracers in the OSIW (<1000 m depth).[76,77] The outflow of the OSIW carries 0.03–0.18 Pg C y^{-1} to the intermediate layer of the North Pacific Ocean.[10,73] This is a substantial amount compared with the total inventory of 0.18 ± 0.08 Pg C in this basin,[78] and accounts for approximately 10% of the annual accumulation of anthropogenic CO_2 in the North Pacific Ocean.[73,74] This active outflow makes the Sea of Okhotsk a small reservoir of anthropogenic CO_2, and is the mechanism by which other anthropogenic gases (i.e. CFCs, N_2O, etc.) are also transported to waters deeper than 300 m in the North Pacific Ocean, which contains little anthropogenic gases. An additional but smaller contribution is the import of water loaded with anthropogenic CO_2 from the East/Japan Sea into the intermediate layer of the Sea of Okhotsk.[19] The salty Soya Warm Current absorbs anthropogenic CO_2 as it flows northward within the East/Japan Sea and enters the Sea of Okhotsk, where it becomes sufficiently dense to sink into the intermediate layer (σ_θ > 26.8) in winter. The amount of anthropogenic CO_2 transported via this mechanism is only 20% of that of the dense shelf water resulting from sea ice formation.[19]

The in situ formation of dense water in the Sea of Okhotsk, and its transport to the interior and to the intermediate North Pacific Ocean may be influenced by climate change. Several studies have indicated that the temperature of the OSIW has increased since the 1950s, and the warming rate (∼0.6 °C per 50 years at 27.00 σ_θ; Fig. 7a) of the OSIW[30,79,80] is much higher than the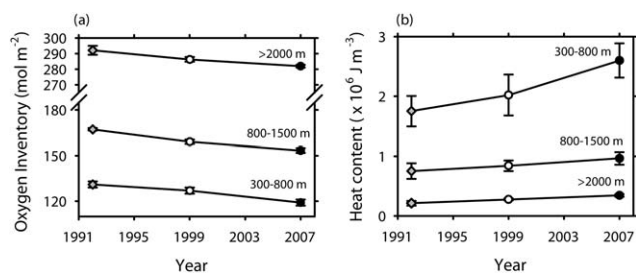 global rate.[81,82] This trend of warming has been accompanied by a tread of decreasing dissolved O_2 content in the OSIW (Fig. 7b).[30] Furthermore, these trends appear to extend to the northwestern part of the North Pacific Ocean, along the path of the water mass that originates in the Sea of Okhotsk. It has been suggested that these changes in the OSIW are caused by declining production of dense water on the northwestern shelf of the Sea of Okhotsk.[30,80] However, as reliable estimates of dense water production are not yet available, the evidence for declining dense water formation is circumstantial. The substantial increase in air temperature during the past 50 years suggests the likelihood of a reduction in dense water formation, because air temperature variations are highly correlated with the sea ice extent.[30] As the residence time of the OSIW is only several years,[72,83] a weakening of vertical ventilation in the Sea of Okhotsk may profoundly change the properties of the OSIW and also the rate of outflow to the North Pacific intermediate layer. The weakening ventilation of the OSIW since 1970 has also resulted in a decrease in O_2 concentration in the NPIW downstream of the Sea of Okhotsk.[84,85] As the Sea of Okhotsk is the key source region for ventilation of the NPIW, weakening of the OSIW ventilation in the future could be accompanied by similar weakening of the NPIW ventilation. Thus, variations in the formation of OSIW are probably key factors influencing variations in the NPIW.

3.4. The East/Japan Sea

The East/Japan Sea is connected to the western North Pacific Ocean by three shallow straits (<150 m depth). The formation of deep water on the continental shelf and the slope of Vladivostok, Russia is a key circulation feature of the East/Japan Sea (Fig. 2d).[86–88] Another important feature of the East/Japan Sea is its weak vertical stability relative to the open ocean and the other marginal seas described above.[29] The deep water formation, enhanced by the anomalous weak stability of the East/Japan Sea, leads to the formation of an active deep convection system whereby the surface water loaded with anthropogenic CO_2 is effectively transported to the interior of the basin. In addition, unlike the other marginal seas discussed above, the East/Japan
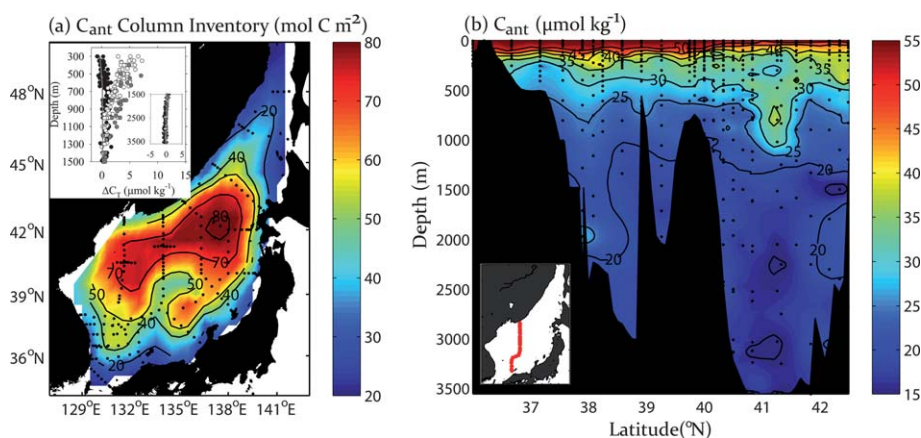
Fig. 8 (a) Water column anthropogenic CO_2 (C_{ant}) inventory per unit area (mol C m^{-2}) in the East/Japan Sea, as of 1999. The inset shows the amounts of C_{ant} accumulated during the periods 1992–1999 (open circles) and 1999–2007 (solid circles) as a function of depth. The gray circles denote data within the anticyclonic eddies. (b) C_{ant} (μmol kg^{-1}) in the section indicated in the inset. Redrawn using data from ref. 6 and 7.

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Fig. 9 Changes in (a) water column oxygen inventories (mol m^{-2}) and (b) heat content (10^6 J m^{-3}) in the upper and lower Proper Water (300–800 m and 800–1500 m, respectively) and Deep Water (>2000 m) in the Japan Basin during the period 1992–2007. Error bars represent one standard deviation from the mean. Redrawn using data from ref. 7.

Sea has no exchange of intermediate and deep waters (containing anthropogenic CO_2) with the adjacent western North Pacific Ocean, and thus does not lose anthropogenic CO_2 to this water body.

As a consequence of the three features described above, the East/Japan Sea may be a significant reservoir for anthropogenic CO_2. Direct observations indicate that anthropogenic CO_2 has penetrated into the bottom (up to 3500 m) of the basin, where its concentration in near bottom waters reaches 10–15 μmol kg^{-1}.[6] The greatest water column inventory of anthropogenic CO_2 has been recorded in the Japan Basin, with a mean value of 80 mol C m^{-2}, referenced to 1999 (Fig. 8).[6] This is much higher than the 20–30 mol C m^{-2} typically found at similar latitudes in the adjacent North Pacific Ocean.[63] This large difference in the water column inventory can be attributed to the sinking of newly formed water (containing anthropogenic CO_2) into the interior of the Japan Basin, whereas at the same latitude in the North Pacific Ocean the anthropogenic CO_2 does not penetrate beyond 1500 m because of the absence of deep water formation.[63]

In contrast to the other marginal seas described above, the overturning circulation in the East/Japan Sea is likely to be more vulnerable to minor oceanic and atmospheric perturbations because the vertical stability of this water body is approximately two orders of magnitude lower. Observations indicate that continual warming of the East/Japan Sea waters below the permanent thermocline has occurred since the 1960s.[29] Over the period 1969–2007 the temperature increase below 2000 m was approximately 0.05 °C, which exceeds the global warming trend of 0.037 °C between 1955 and 1998.[82] The dissolved O_2 concentration in the same water layer also decreased during the same period. The cause of this is probably a shift in ventilation involving weaker formation of deep and bottom water, and a strengthening of intermediate water formation.[89–92]

Although available carbon data (from surveys in 1992, 1999 and 2007) do not cover the entire warming period (1960s onward), they enable evaluation of changes in the rate of the accumulation of anthropogenic CO_2 in the East/Japan Sea over the survey period (1992–2007) in response to surface ocean perturbations. The mean uptake rate of anthropogenic CO_2 by the East/Japan Sea was 0.3 ± 0.2 mol C m^{-2} y^{-1} for the period 1999–2007, which is in marked contrast to the rate of 0.6 ± 0.4 mol C m^{-2} y^{-1} for the period 1992–1999 (inset in Fig. 8).[7] The striking feature is that virtually no increase of anthropogenic

CO_2 was found in waters deeper than 300 m (mean winter mixed layer depth) for the period 1999–2007. The rapid and substantial reduction in the uptake rate of anthropogenic CO_2 by the East/Japan Sea in this period is likely to be because of considerable slowing of water column ventilation, by which the anthropogenic CO_2-charged surface water is transported to the interior of the East/Japan Sea.[7]

The progressive decrease in the O_2 concentration in the Japan Basin is key evidence for weakening of water column ventilation, given the constant consumption of O_2 due to oxidation of organic matter settling from the surface. The rate of decrease in the water column O_2 inventory of the upper Proper Water (300–800 m) was two-fold higher for the period 1999–2007 than for the period 1992–1999 (Fig. 9a).[7] This water layer contains 80% of the total anthropogenic CO_2 that has entered the East/Japan Sea since 1992. The increased rate of decrease in the water column O_2 inventory during the period 1999–2007 (relative to that during the period 1992–1999) may be evidence for comparable weakening of the upper Proper Water ventilation over the transition period, and consequently of insignificant transport of anthropogenic CO_2 from the surface to the upper Proper Water.[7] An important issue that remains to be clarified is the cause of the waning of water column ventilation over the past 15 years. Water column warming is a distinct possibility. Relative to 1992–1999 the two-fold increase in the rate of heat content increase in the upper Proper Water for the period 1999–2007 is consistent with a reduction in the water column O_2 inventory in this water layer during the same period (Fig. 9b).[7] This trend of increasing heat content is likely to have resulted in weakening of water column ventilation. However, elucidation of the governing mechanism(s) is presently far from being achieved.

The East/Japan Sea is well ventilated to the bottom over decadal time scales, and thus the anthropogenic CO_2 content in deep and bottom waters is tied to surface water conditions with similar delay periods. However, because the formation of sea ice is the source of deep and bottom waters in the East/Japan Sea, future climatic changes that greatly reduce or eliminate sea ice in the East/Japan Sea could have profound impacts on the anthropogenic CO_2 content of its abyssal waters. Although the impact of the East/Japan Sea processes on North Pacific water properties is not firmly established, it should not be overlooked. The decreasing salinity and cooling processes within the East/Japan Sea may affect the formation of NPIW by modifying the properties of the outflow entering the Sea of Okhotsk. Changes in NPIW formation directly impact the amount of anthropogenic CO_2 that is transported from the Sea of Okhotsk to the North Pacific Ocean.

4. Other marginal basins without overturning circulation systems

In addition to the four marginal seas discussed above, several other marginal seas are worthy of consideration because their storage and transport of anthropogenic CO_2 to adjacent major basins may be substantial. There are few studies concerning the anthropogenic CO_2 stored in these basins and how these stores have evolved over time, but the physical nature of individual basins potentially influencing the sequestration of anthropogenic CO_2 can be considered.

The East China Sea

The East China Sea has an extensive continental shelf accounting for two-thirds of its area (yellow shading in Fig. 2), and is biologically productive because it receives large amounts of nutrients from the Yangtze and Yellow Rivers. Although it is highly undersaturated with respect to the anthropogenic CO_2,[93,94] the anthropogenic CO_2 storage of the East China Sea was only 0.07 ± 0.02 Pg C (as of 1994)[10] due to the absence of overturning circulation and deep basins. The anthropogenic CO_2 has penetrated to only about 600 m into the deepest basin.

The South China Sea

The South China Sea is the largest marginal sea and has deep basins (up to $\sim$5500 m) in the central and northeastern regions (blue shading in Fig. 2). As there is no intermediate and deep water formation in the South China Sea, the anthropogenic CO_2 has penetrated to only about 1000–1500 m depth, and its basin-wide inventory is 0.43–0.60 Pg C, as of 1994.[10,95] The greatest water column inventory of anthropogenic CO_2 has been recorded in the northern basin, with a mean value of 16.6 mol C m^{-2}.[96] This figure is similar to the inventory values typically observed in the adjacent Pacific Ocean.

The Bering Sea

The Bering Sea comprises a broad shelf and a deep basin, of approximately equal surface areas (green shading in Fig. 2). The anthropogenic CO_2 has penetrated to 1000 m, but more deeply in the eastern and southern regions relative to that of the Kamchatka Peninsula. The anthropogenic CO_2 concentration at 1000 m is approximately 5 μmol kg^{-1}.[97] Other anthropogenic gases (including CFCs and tritium) have similar depth distribution patterns. The Bering Sea contained 0.21 ± 0.05 Pg C of anthropogenic CO_2, as of 1980.[10] Although the inventory is small, the transport of Bering Sea water to the North Pacific may feed the NPIW with anthropogenic CO_2,[98] although this and a possible connection with the Arctic have not been fully explored. If such transport occurs it could be vulnerable to climate change. An additional factor of potential future concern is the carbonate deposits on the Bering Sea shelves. The saturation horizon for aragonite is very shallow in the Bering Sea, and further oceanic uptake of anthropogenic CO_2 could, by the middle of this century, drive shelf waters to undersaturation conditions with respect to the aragonite and high-magnesium calcite.[99] The dissolution of shelf carbonates will increase the seawater A_T and help naturalize anthropogenic CO_2.

North Sea

The North Sea is enclosed by three land masses (the UK, the European continent and the Scandinavian Peninsular) but is open to the north where it exchanges water with the North Atlantic Ocean (orange shading in Fig. 2). The North Sea is a strong net sink for anthropogenic CO_2 throughout the year; the sink is particularly strong in spring and summer but is weak in fall and winter.[100] The southern part of the North Sea acts as a net source for anthropogenic CO_2 throughout the year. The basin-wide CO_2 uptake by the North Sea is 8.5×10^{12} g C y^{-1} (or 1.38 mol C m^{-2} y^{-1}).[100] A significant fraction (93%) of the CO_2, either absorbed from the atmosphere or produced by biological process in the water column, is exported to the intermediate layer of the North Atlantic Ocean. Therefore, the North Sea efficiently pumps CO_2 from the atmosphere to the North Atlantic Ocean *via* the interior of the North Sea.[101]

Red Sea

The Red Sea is enclosed by the Asian and African continents, but has a deep and narrow connection (running northwest to southeast) to the Indian Ocean (Gulf of Aden; pink shading in Fig. 2). The significant evaporation from the Red Sea results in a Mediterranean-type water circulation involving a surface inflow above a subsurface outflow. Radiocarbon (^{14}C) data have shown that the Red Sea is fully ventilated only over several decades.[102] The anthropogenic CO_2 signal was detected at all depths (maximum at 600 m) in the northern part of the Red Sea.[103] The outflow from the Red Sea transfers anthropogenic CO_2 to the northern Indian Ocean.[104] However, because of the high pCO_2 values in its southern region, the Red Sea constitutes a net CO_2 source to the atmosphere (1.2–4.8×10^{12} g C y^{-1}).[105–107] It is not known whether the anthropogenic CO_2 has increased the net outgassing from this region, but if so this would represent a decrease in its anthropogenic CO_2 storage efficiency.

The Black Sea

The Black Sea is connected to the Mediterranean Sea by the Bosphorus Strait, through which the saline water moves to the Black Sea (dark blue shading in Fig. 2). This saline water flows across the continental shelf and into abyssal waters. During transit it mixes with fresher but colder intermediate water, and then spreads out in thin layers into the Black Sea basin.[108] The overlying less saline water, maintained by freshwater input, is strongly stratified from the saltier and colder intermediate water. The strong stratification and long residence time of Black Sea deep water (>625 years below 500 m) prevents CFCs from penetrating to more than 500 m depth.[109] Therefore, it is expected that anthropogenic CO_2 is also confined to the upper layer of the Black Sea. According to *Goyet et al.*[110] the air-to-sea flux of CO_2 in the Black Sea is approximately 7.3 mol C m^{-2} y^{-1} in summer, and this relatively high flux may be caused by the high surface A_T and biological productivity.[111]

The Gulf of Mexico

A significant regional and temporal variability in CO_2 flux across the air–sea interface occurs in the Gulf of Mexico (light purple shading in Fig. 2), because factors affecting CO_2 flux (including river input and biological productivity) vary considerably in space and time. In general, the river plume area acts as a sink for CO_2 (approximately 1.5 mol C m^{-2} y^{-1}),[11] whereas the most offshore water is a source of CO_2 (1.7 mol C m^{-2} y^{-1}) to the atmosphere.[11,112] The shallow penetration (<1000 m depth) of CFCs into the Gulf of Mexico indicates the absence of active overturning circulation, which further suggests little or no anthropogenic CO_2 in deep waters.[113] However, the connection to the Atlantic Ocean by the Florida Current may mean that

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anthropogenic CO_2 is transported into the Gulf of Mexico at intermediate depths.

5. Impacts of human perturbations on the absorption of anthropogenic CO_2 by global marginal seas

Human-induced perturbations are diverse[12,14,114] and can interact, and thus their relative impacts on oceanic absorption of anthropogenic CO_2 may vary considerably in individual marginal seas. With the data available it is not possible to assess the impact of multiple interacting perturbations on the absorption and storage of anthropogenic CO_2 in the marginal seas reviewed in the preceding sections. Therefore, this review focuses on the individual effects of three well established perturbations—nutrient input, river discharges and carbonate chemistry—on the absorption and storage of anthropogenic CO_2 in marginal seas.

As a consequence of increasing fertilizer use, increased nutrient fluxes into marginal seas may be stimulating organic carbon production by phytoplankton, thereby enhancing CO_2 absorption from the atmosphere.[115–119] This effect is potentially significant if the organic carbon resulting from these excess nutrients is either permanently stored in the sediments of marginal seas or exported to the interior of adjacent open oceans. Organic carbon buried in the sediments of marginal seas is further subject to anaerobic degradation, which generates A_T through denitrification and sulfate reduction, thereby increasing the CO_2 buffer capacity of seawater in the marginal seas.[9] Such anaerobic A_T generation is potentially significant in many marginal seas and acts on a time scale similar to that of oceanic uptake of anthropogenic CO_2. This process in marginal seas allows direct interaction between the sedimentary environment and the overlying atmosphere; in the deep ocean, by contrast, this interaction occurs over extended time scales ($\sim$1000 years). At a global scale, anaerobic A_T generation could account for as much as 60% of CO_2 uptake in shelves and marginal seas.[9]

Another perturbation worthy of consideration is changes in fresh water discharge resulting from dam construction and agricultural use of fresh water. Changes in fresh water discharge could modify nutrient inputs to marginal seas, and their buoyancy and upwelling patterns. The interactions of these factors should be investigated to enable assessment of the oceanic uptake of anthropogenic CO_2 in the marginal seas described here. Changes in freshwater discharge could also cause changes in the export of terrestrial A_T (mainly through carbonate and bicarbonate ions) to the marginal seas. The terrestrial flux of A_T can have a significant impact on seawater A_T,[120–123] and so can influence the uptake of anthropogenic CO_2 by marginal seas. The human-induced perturbations described here are likely to influence the absorption of anthropogenic CO_2 by most marginal seas and its subsequent transport to adjacent basins. However, an understanding of how these perturbations influence the overall uptake efficiency of anthropogenic CO_2 is only now beginning to be developed for most marginal seas.

6. Conclusions

The four key marginal seas discussed here—the Arctic Ocean, the Mediterranean Sea, the Sea of Okhotsk, and the East/Japan Sea—each stores proportionally more anthropogenic CO_2 than the global ocean. Previous estimates of global ocean storage of anthropogenic CO_2 have been derived from scale-up open ocean inventories based on the volume of the marginal seas.[5,75] This review suggests that this scaling has underestimated the contribution of the marginal seas and the net global ocean anthropogenic CO_2 inventory. The exception is the Arctic Ocean where the anthropogenic CO_2 content was overestimated because of limited CFC data.

Three of the seas examined in detail (the Arctic Ocean, the Mediterranean Sea, and the Sea of Okhotsk) contribute significant anthropogenic CO_2 to their adjacent major basins, although the full extent remains to be clarified. For all four of the marginal seas discussed in this paper, the major conclusions are that a key process in determining the anthropogenic CO_2 uptake efficiency is overturning circulation; however, the intensity of this process appears to have weakened in recent years, which has affected the uptake of anthropogenic CO_2. Furthermore, variation in the intensity of overturning circulation is intimately linked to global- and/or regional-scale climate change. It is likely that these findings can be extrapolated to the global ocean, but this remains to be determined. Integration of newly acquired data from ongoing programs (including the Climatic Variability and Predictability Repeat Hydrography program) with earlier data will enable the links between marginal seas and the major ocean basins to be explored, and facilitate assessment of whether the findings for the marginal seas are likely to be reflected in coming decades in the global ocean.

In contrast, marginal seas with no active overturning circulation systems store less anthropogenic CO_2 per unit area than the four key marginal seas (the Arctic Ocean, the Mediterranean Sea, the Sea of Okhotsk, and the East/Japan Sea). As these marginal seas are generally located in the vicinity of populated continents, and are heavily influenced by large tributaries, human-induced perturbations may have a significant impact on their absorption of anthropogenic CO_2. Ongoing observations will be necessary to provide information on how interactions among multiple perturbations influence the absorption of anthropogenic CO_2 by these marginal seas, and its subsequent transport to adjacent basins.

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