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Wastewater alkalinity addition as a novel approach for ocean negative carbon emission

Wei-Jun Cai[1,*] and Nianzhi Jiao[2,*]

[1]School of Marine Science and Policy, University of Delaware, Newark, Delaware 19716, USA

[2]Carbon Neutralization Innovation Research Center, and the Joint Lab for Ocean Research and Education at Shandong University, Dalhousie University, Xiamen University, Xiamen 361005, China

[*]Correspondence: wcai@udel.edu (W. C.); jiao@xmu.edu.cn (N.J.)

Anthropogenic CO_2 emissions have greatly increased atmospheric CO_2 contributing to global warming and leading to ocean acidification (Figure 1). As reflected in the recent IPCC report, the scientific community's consensus is that emissions reductions alone are not sufficient or timely enough to avoid a global warming catastrophe. Thus, negative carbon emission technologies are needed to avoid atmospheric CO_2 overshoot scenarios and limit global warming to less than 2 °C by the end of this century per the Paris Agreement. Due to the urgency and scale of the issue, multiple negative emission technologies should be evaluated and adopted with broad community involvement to address our society's pressing climate crisis. The goal is to remove at least 10 Gt-CO_2/yr from the atmosphere by the mid to-late century,[1] which is more than the current annual anthropogenic CO_2 uptake by the global ocean (Figure 1). Among various Ocean Negative Carbon Emission (ONCE) approaches or ocean-based Carbon Dioxide Removal (CDR) technologies, Ocean Alkalinity Enhancement (OAE) is an approach that will decrease sea surface pCO_2 via the addition of alkaline materials and promote CO_2 uptake from the atmosphere. Additionally, as the oceanic dissolved inorganic carbon (DIC) reservoir is nearly 50 times the atmospheric CO_2 content, the sequestered CO_2 can remain in the ocean DIC pool as bicarbonate (HCO_3^-) for centuries. OAE is viewed with high confidence under the efficacy criterion and medium on environmental risk in the recent report by the *National Academies of Sciences, Engineering, and Medicine*.[2]

Several fundamental questions have not yet been answered regarding OAE. These include “how realistically and effectively can highly alkaline source materials such as NaOH and $Ca(OH)_2$ mix into natural seawater without forming substantial secondary mineral ($CaCO_3$) precipitation” and “how realistically will readily available carbonate and silicate minerals dissolve in seawater”? This is because ocean surface water conditions are supersaturated with respect to $CaCO_3$ minerals and unfavorable to the dissolution of silicate minerals such as olivine.[3] Thus, how to appropriately and efficiently add alkaline materials to the ocean to achieve OAE and CDR is a tremendous challenge before us.

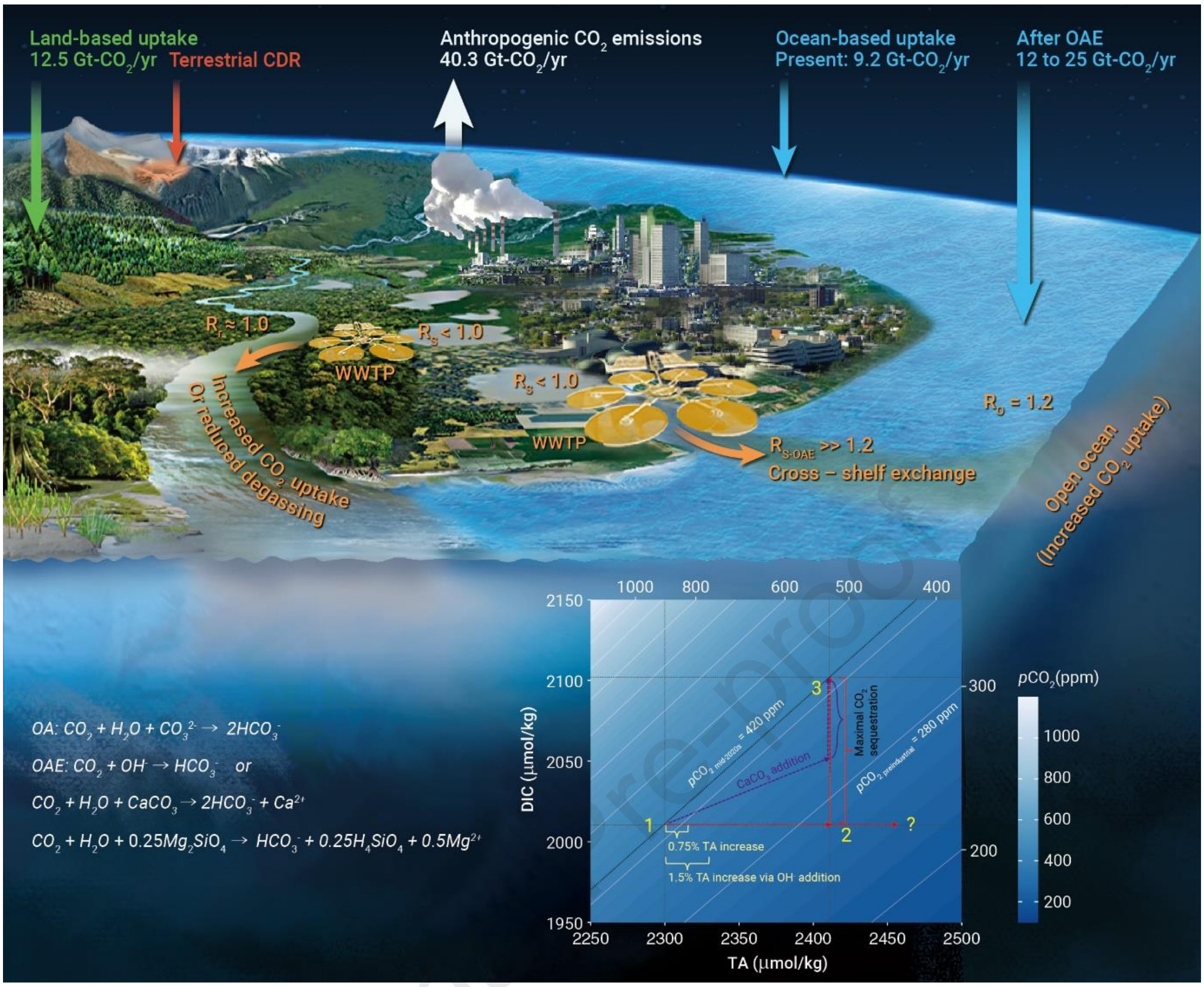

Figure 1. Conceptualization of adding alkaline materials to the effluent of Wastewater Treatment Plants (WWTPs) to achieve Ocean Alkalinity Enhancement (OAE) and Ocean carbonate chemistry principles (the inserted part). R is the ratio of total alkalinity (TA = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$) to DIC, the sum of all dissolved inorganic carbon species. Rivers usually have $R_r \approx 1.0$. Sewage has $R_S < 1.0$, but after adding alkaline materials, sewage can have $R_{S\text{-}OAE} >> 1.2$. Increasing the oceanic TA to DIC ratio (R_o) by 2.5% from 1.17 to 1.2 can achieve the ocean-based CDR goal with an initial flux of 3 and a final flux of 16 Gt-CO$_2$/yr in addition to the current 9 Gt-CO$_2$/yr (i.e., a total flux of 12-25 Gt-CO$_2$/yr). The targeted global ocean CO$_2$ uptake flux of 12-25 Gt-CO$_2$/yr can be achieved by raising the ocean surface TA by 0.75-1.5% and reducing pCO$_2$ by 25-50 ppm. The current CO$_2$ emission and uptake fluxes are based on ref 2. OA stands for Ocean Acidification. In the inserted part, red dotted lines (from point 1 to 2 and to 3) represent OAE schemes via the addition of NaOH followed by CO$_2$ uptake from the atmosphere. The purple lines represent addition of CaCO$_3$. A maximal increase of TA by 4.7% via NaOH addition would decrease sea surface pCO$_2$ to 280 ppm and increase pH to 8.17 (year 1750 or preindustrial conditions). A 0.75%, 1.5% and 3.0% TA enhancement will bring ΔpCO$_2$ (sea – air) to -25, -50, and -100 ppm, respectively and the air-sea flux to -1.68, -4.19, and -8.39 mmol/m^2/d, respectively. These fluxes are scaled up to derive global ocean CO$_2$ uptake fluxes, on which a 2.57 Gt-CO$_2$/yr preindustrial river flux is added to the net flux to derive the final global ocean anthropogenic CO$_2$ uptake fluxes.

SEWAGE ALKALINITY ADDITION

We postulate here the novel idea that OAE can be applied to safely, permanently, and cost-effectively sequester atmospheric CO_2 using Wastewater Treatment Plant (WWTP) effluent (Figure 1). As wastewater (sewage) has low pH, high pCO_2, and high concentrations of organic acids, it can be used to deliver strong bases without substantial secondary precipitation (i.e., $CaCO_3$) and can dissolve abundant and inexpensive olivine and $CaCO_3$ minerals in dissolution-favorable conditions. More importantly, the added alkalinity can be exported offshore by river plumes and ocean currents to achieve OAE and CDR at scale.

Each year, nearly 1000 km^3 of wastewater is generated around the world with about 300 km^3 discharged as municipal wastewater and over 600 km^3 as industrial wastewater.[4] Sewage has a high DIC concentration of 3000-5000 μmol C/kg and a pCO_2 value of over 10,000 parts per million (ppm), the release of which may lead to CO_2 degassing from and acidification of coastal waters.[5] While opportunities for carbon capture and utilization during wastewater treatment have received extensive attention,[4] the potential for using wastewater as an effective means for the production and delivery of alkalinity to the ocean (i.e., OAE) for CDR has not been explored and is the focus of this paper.

OCEAN CARBONATE CHEMISTRY

With the atmospheric CO_2 increases from the preindustrial level of 280 ppm to nearly 420 ppm at present, CO_2 entered the ocean, leading to Ocean Acidification (OA) (Figure 1). As a result, ocean DIC concentrations increased, but TA did not change. In contrast, under the OAE strategy, TA and DIC increase at a ratio of 2:1 for the case of carbonate mineral addition ($CaCO_3 + CO_2 \rightarrow 2HCO_3^-$). And when NaOH or $Ca(OH)_2$ is added ($CO_2 + OH^- \rightarrow HCO_3^-$), TA increases with no DIC change, which subsequently promotes a strong CO_2 uptake from the atmosphere. Thus, the latter is a more efficient pathway for ocean-based CDR than $CaCO_3$ dissolution (Figure 1).

An important distinction between OAE and OA lies in the levels of pCO_2 and pH change. In the OA consideration, the change or modification is from 280 ppm to about 1000 ppm (early next century business-as-usual prediction), corresponding to a pH decrease from 8.2 to 7.7. In contrast, in the OAE consideration, the need to reduce sea surface pCO_2 in the open ocean is small, well within recent historical levels. For example, on a global ocean scale and, assuming an equilibrium between surface ocean and the atmosphere, if we can reduce, on average, sea surface pCO_2 by a total of 25, 50, and 100 ppm to 395 ppm (mid 2010s level), 370 ppm (early 2000s) and 320 ppm (late 1960s), we can achieve a CO_2 uptake rate of 13.5, 24.4 and 46.2 Gt-CO_2/yr, respectively, assuming that atmospheric pCO_2 will be stabilized at 420 ppm (mid-2020s) (Figure 1). This is equal to or higher than the global CDR goal of removing at least 10 Gt-CO_2/yr. Though it is unlikely that pCO_2 can (or needs to) be reduced by 50-100 ppm everywhere in the global surface ocean and adding alkalinity may take decades, we clearly do not need to reduce sea surface pCO_2 or modify seawater pH greatly to reach the CDR goal. As illustrated in Figure 1, this pCO_2 reduction can be induced by raising sea surface TA by <1-3%. Thus, in the ocean where most CO_2 uptake occurs due to its vast area, the modification of carbonate chemistry will be minimal, and the likely environmental, biological, and ecosystem impacts are expected to be small. However, numerical models at both regional and global scales should be carried out to simulate the amount, rate, location, and duration of TA additions and assess the efficacy and impacts of this proposed CDR strategy.

ADVANTAGES OF OUR APPROACH

A sewage-delivered OAE approach is a novel concept in the ocean-based CDR family and has the following advantages over other OAE approaches. (1) Direct application of NaOH and $Ca(OH)_2$ into the open ocean water will unavoidably induce $CaCO_3$ or even $Mg(OH)_2$ precipitation and alkalinity loss at the release points, while low pH wastewater may allow us to avoid this problem. (2) Most ocean waters are supersaturated with respect to $CaCO_3$ minerals and are dissolution-unfavorable to silicate minerals no matter how fine they are pulverized. Low pH and organic acid-rich wastewaters provide an ideal site where these minerals may dissolve at meaningful rates for CO_2 sequestration purposes. (3) Coastal waters are often CO_2 sources to the atmosphere and have suffered from severe seasonal ocean acidification due to the synergistic effects of anthropogenic and respiration-induced CO_2. Application of alkaline materials in WWTPs and their effluents will reduce CO_2 release and ameliorate acidification in estuaries, providing co-benefits for environmental health and fisheries. (4) Applying mineral alkaline sources to coastal waters is economically more viable than transporting them to the open ocean, because transportation of minerals using ~1000 ships is a major factor in the cost and energy consumption estimation of the known OAE approaches.[2] While we advocate the sewage-enabled OAE approach, we strongly recommend that impacts on environments, organisms, and ecosystems be carefully evaluated because coastal zones have already been facing multiple environmental and climate-related stressors and are more vulnerable than the open ocean.

CONCLUDING REMARKS

Using sewage and other low pH coastal waters as a means to add alkalinity to the ocean is novel and has many advantages for achieving ocean alkalinity enhancement and CO_2 removal with the co-benefit of ameliorating ocean acidification in both the coastal and open ocean. Regional and global scale numerical model simulations should be used to more fully evaluate the efficacy of this proposed approach in ONCE or ocean CDR while water quality and biological impacts in coastal environments should be monitored and studied.

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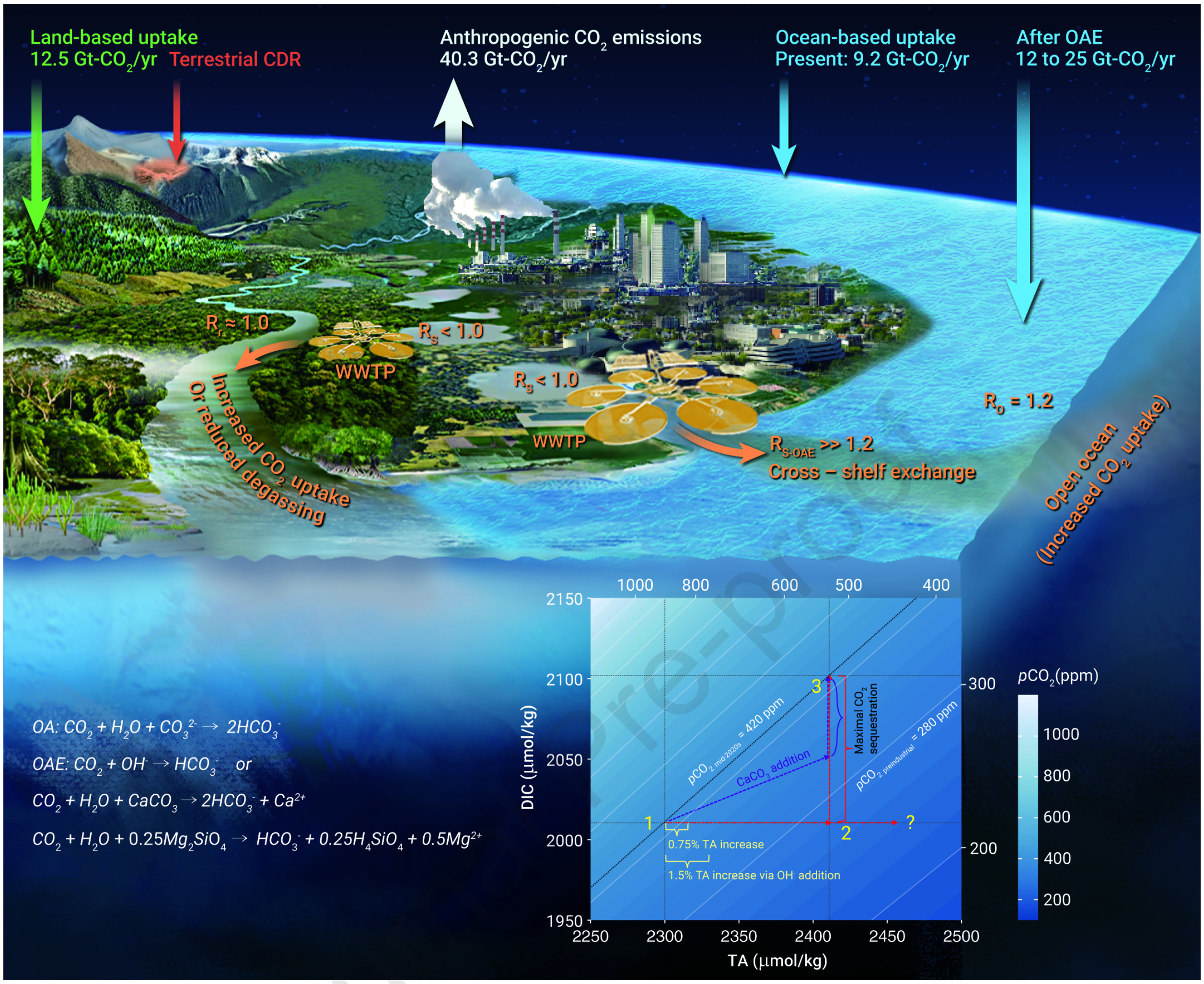
DECLARATION OF INTERESTS

The authors declare no competing interests.


Land-based uptake
12.5 Gt-CO_2/yr
Terrestrial CDR
Anthropogenic CO_2 emissions
40.3 Gt-CO_2/yr
Ocean-based uptake
Present: 9.2 Gt-CO_2/yr
After OAE
12 to 25 Gt-CO_2/yr
$R_r \approx 1.0$
$R_s < 1.0$
WWTP
$R_s < 1.0$
WWTP
Increased CO_2 uptake
Or reduced degassing
$R_{S\text{-}OAE} >> 1.2$
Cross – shelf exchange
$R_o = 1.2$
Open ocean
(Increased CO_2 uptake)
OA: $CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^-$
OAE: $CO_2 + OH^- \rightarrow HCO_3^-$ or
$CO_2 + H_2O + CaCO_3 \rightarrow 2HCO_3^- + Ca^{2+}$
$CO_2 + H_2O + 0.25Mg_2SiO_4 \rightarrow HCO_3^- + 0.25H_4SiO_4 + 0.5Mg^{2+}$
1000
800
600
500
400
2150
2100
2050
2000
1950
DIC (μmol/kg)
300
200
pCO_2(ppm)
1000
800
600
400
200
$pCO_{2\ \text{mid-2020s}}$ = 420 ppm
3
Maximal CO_2 sequestration
$CaCO_3$ addition
$pCO_{2\ \text{preindustrial}}$ = 280 ppm
1
2
?
0.75% TA increase
1.5% TA increase via OH^- addition
2250
2300
2350
2400
2450
2500
TA (μmol/kg)