# Initial Outline of OAE CDR MRV: Concepts and Needs

G. Rau, S. Rackley, W. Burt, S. Tahmasebi, O. Sadoon, B. Kielly, M. Kelland
Planetary Technologies, Inc., Dartmouth, Nova Scotia, Canada
Contact: greg@planetarytech.com
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**Purpose:** Contribute to a living, community document for developing methods of monitoring, recording and verifying (MRV) of carbon dioxide removal (CDR) achieved by Ocean Alkalinity Enhancement (OAE) that in its final form would be acceptable to stakeholders, governance bodies and carbon credit markets. Specifically, develop methods that quantify the net reduction of atmospheric $CO_2$ burden by OAE, the duration of this reduction and its environmental safety with a given level of precision and accuracy.

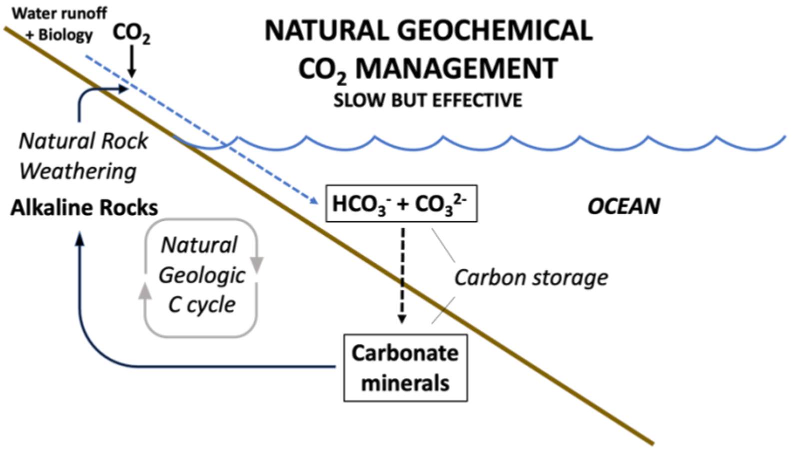
**Outline:**
1) OAE rationale - Ocean alkalinity and how it relates to atmospheric $CO_2$ management
2) Methods of OAE - Types of alkalinity, modes of application and effect on air $CO_2$
3) OAE MRV Concepts and Issues - Biological and chemical measurements and limitations
4) Further MRV Specifics (Outline)
5) Illustration of Possible Seawater Chemistry Responses

## 1) OAE Rationale

In effect, alkalinity is the ability of a solution to neutralize acid, that ability being imparted by the presence of one or more chemical bases. In natural seawater these bases are present primarily in the form of bicarbonate (82%), carbonate (15%) anions (with much smaller quantities of borate, hydroxide and other anions) as balanced by cations other than $H^+$. Alkaline seawater bicarbonate and carbonate ions comprise some $37.8 \times 10^{12}$ t C or about 88% of the Earth's surface carbon that is in communication with the atmosphere. Atmospheric $CO_2$ is in quasi-equilibrium with surface seawater bicarbonate and carbonate ions, and the roughly 50:1 partitioning of ocean/atmosphere C speaks to the importance of seawater alkalinity in chemically ensuring that most C is in the ocean and not the atmosphere. If seawater alkalinity was reduced by 10X, atmospheric $CO_2$ would be >100X higher than at present. It therefore follows that actions that increase the partitioning of C out of the atmosphere and into the ocean via increasing ocean alkalinity would be beneficial to global $CO_2$ and climate management. It would also be helpful in countering ocean acidification because alkalinity addition elevates seawater pH. OAE therefore seeks ways of cost effectively, safely and verifiably reducing the $CO_2$ burden in the atmosphere while also helping neutralize ocean acidity.

The idea of purposely adding alkalinity to the ocean for the preceding purposes is inspired by the fact that this is the primary way Mother Nature consumes $CO_2$ and rebalances ocean chemistry on geologic time scales (Archer et al 2009). Here, globally abundant alkaline rocks react with $CO_2$ and water to produce dissolved, alkaline bicarbonates and carbonates that eventually are added to the ocean via river discharge. This explains why seawater is a naturally alkaline medium containing the majority of carbon on the Earth's surface. On 100,000 yr. time scales this alkalinity eventually precipitates from seawater as calcium carbonate thus entering the geologic C cycle (Figure 1). Can this ocean alkalization be safely and cost-effectively speeded up so that CDR is effected on human-biologic rather than geologic time scales?

Fig. 1:



## 2) Methods of OAE CDR

There are 2 types of alkalinity to consider for OAE. The first of these is the use of $CO_2$-reactive bases, that is, bases that when added to the ocean directly react with dissolved $CO_2$ to form seawater bicarbonates and carbonates, Examples of either natural or synthetic $CO_2$-reactive bases include:

Hydroxides - $Mg(OH)_{2aq} + 2CO2 \text{---->} Mg^{2+} + 2HCO_3^-$ 1)
Oxides - $CaO_s + H_20 \text{--->} Ca(OH)_{2aq} + 2CO_2 \text{--->} Ca^{2+} + 2HCO_3^-$ 2)
Silicates - $Mg_2SiO_{4s} + 4CO_2 + 2H_2O \text{---->} 2Mg^{2+} + 4HCO_3^- + SiO_2$ 3)
Carbonates- $CaCO_{3s} + CO_2 + H_2O \text{---->} Ca^{2+} + 2HCO_3^-$ 4)

Note that due to equilibrium reactions some carbonate ion ($CO_3^{2-}$) is also formed with the above, aqueous end products. This reduces somewhat the 1:1 molar ratio of $CO_2$ consumed:alkalinity added implied in the above reactions. Note also that adding one mole of a base composed of a divalent metal (e.g., $Mg^{2+}$, $Ca^{2+}$ above) results in the addition of 2 moles of alkalinity or less if that base is added as a solid and fails to completely dissolve.

Use of mineral silicates and carbonates provide globally abundant and relatively inexpensive alkalinity sources, but exhibit very slow dissolution and reaction rates under natural conditions. On the other hand, metal hydroxides and oxides are rare in nature, but are commonly synthesized and offer much greater reactivity, though with added production cost unless waste streams can be used. Source options and tradeoffs of alkalinity sources for OAE are reviewed in Renforth and Henderson (2017) and NASEM (2021).

The addition of $CO_2$-reactive alkalinity to seawater consumes some fraction of resident dissolved $CO_2$ and converts it to alkaline bicarbonate and carbonate ionic forms. If the alkalinity is added to the ocean in solid rather than dissolved form, then at least some of the solid must dissolve in order to effect OAE and CDR. The addition of $CO_2$-reactive alkalinity can impact atmospheric $CO_2$ in one of 2 ways: 1) it either reduces the degassing of $CO_2$ from the ocean surface to air in regions of the surface ocean where $CO_2$ is supersaturated relative to air (typical of upwelling regions), or 2) it increases the ingassing of $CO_2$ from air $CO_2$ to ocean by undersaturating surface ocean $CO_2$ relative to air. Either way, the atmospheric $CO_2$ burden is lowered by reducing natural, ocean-->air $CO_2$ emissions or by increasing air-->sea $CO_2$ ingassing. The effect on atmospheric $CO_2$ will be most immediate when the alkalization occurs in surface water in direct contact with air and will be delayed (by as much as 1000+ yrs) if the alkalization only occurs in deeper waters or water subducted to the deep ocean (e.g., Fig. 2).

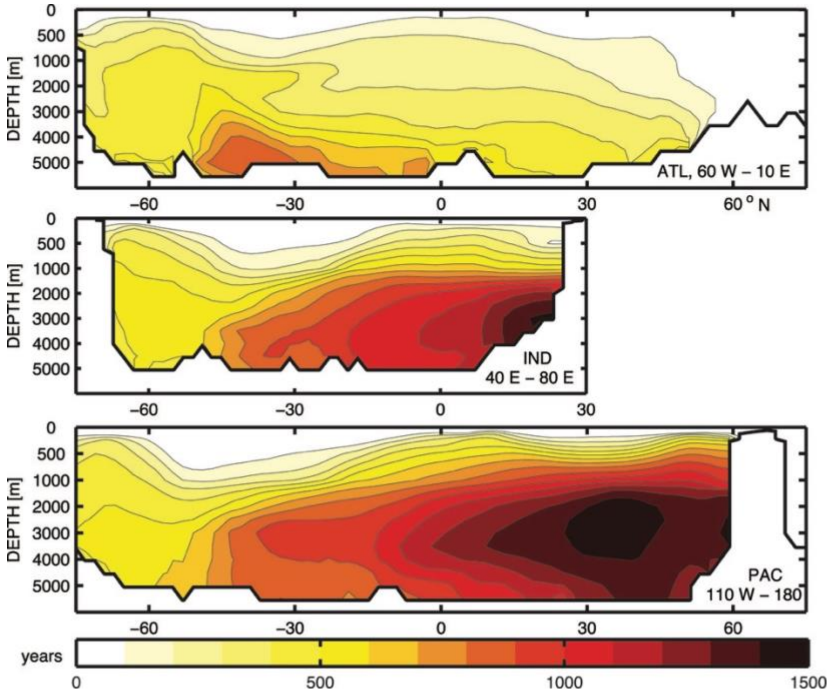


Figure 2. Mean age of seawater vs depth and latitude in the Atlantic, Pacific and Indian Oceans. This is the time since the last exchange with the atmosphere. https://journals.ametsoc.org/view/journals/phoc/42/2/jpo-d-11-043.1.xml

For crediting purposes, evidence of near-term benefit to air $CO_2$ concentration will be most directly found either in an increase in surface seawater DIC or the maintenance of DIC that would otherwise be lowered due to loss of excess seawater $CO_2$ to air. How these can be measured/modeled/estimated and their precision and accuracy form the crux of OAE CDR verification and are discussed in subsequent sections.

*Non-$CO_2$-reactive alkalinity addition* - A second form of alkalinity to consider for ocean addition is that which has already reacted with air $CO_2$ and thus has formed alkaline bicarbonate and carbonate in solution. In this case the addition of this alkalinity does not result in further $CO_2$ capture or $CO_2$ emissions reduction by the ocean, but does provide carbon storage. This mode of OAE is analogous to natural ocean alkalization where rock/$CO_2$ reactions on land/in soils produce carbonated alkalinity that then enters the ocean and is stored (Fig. 1). In the case of artificial OAE, the dissolved bicarbonate and carbonate ions added to the ocean can be derived from atmospheric $CO_2$ or from fossil $CO_2$ emissions where the appropriate carbon crediting can be evaluated/awarded upstream from ocean alkalinity addition. Nevertheless, verification of C storage longevity/security once in the ocean is required.

A conceivable variant of the preceding would be to add solid bicarbonate/carbonate to the ocean that has been derived from upstream air or waste $CO_2$. In this case, while C sequestration would be effected, ocean alkalization will only occur if some or all of the material subsequently dissolves. For example, given that the surface ocean is supersaturated in $CaCO_3$, any solid $CaCO_3$ added here will not dissolve unless under special, local circumstances and, hence, will not enhance ocean alkalinity. However, if this material sinks to ocean depths that are naturally undersaturated (typically >3,000m but can be as shallow as 200m, e.g., N. Pacific Ocean), then dissolution and alkalinity addition will occur there. In general, the deeper the release of alkalinity the longer it will take for that alkalinity to be advected to the ocean surface where it can contact the atmosphere and effect CDR. However, if present, ocean acidification will be immediately decreased in any depth where the added alkalinity is present.

## 3) OAE MRV Concepts and Issues

For all forms of OAE, the subsequent environmental safety of a specific alkalinity addition/enhancement needs to be verified. Such effects include chemical and biological responses to pH, alkalinity, particles (if added) and any elements/compounds that accompany the alkalinity addition. In contrast to the extensive, experimental research on the effects of lowered pH on marine organisms (ocean acidification, citations), much less work has been done on the effects of elevated pH. Generally, the effects have been observed to be neutral to positive (e.g. restoration of marine calcification - Albright et al. 2016), but more research is needed.

Permitting of ocean discharge typically requires a $pH < 9$ (<8.5 in the UK). [Add background on the development of such standards.] Keeping seawater pH below 9 is recommended on chemical grounds considering that dissolved calcium carbonate, a common constituent of seawater, spontaneously precipitates near this pH level. Such precipitation would decrease seawater C storage and increase $CO_2$ levels while generating cloudiness and opacity in seawater. For these reasons protocols are need to insure that OAE CDR applications avoid such precipitation and chemical modification of seawater.

Certainly, any $CO_2$ removal, emissions reduction and/or C storage effected by OAE will be only part of the carbon crediting story. Any fossil $CO_2$ emissions associated with OAE processes (alkalinity extraction, production, refining, distribution, etc.) must be subtracted from the preceding in order to obtain a net atmospheric $CO_2$ benefit and hence C crediting. [[Further discussion needed....]]

*Pre-carbonated alkalinity* - The easiest C crediting for OAE will be when the alkalinity is fully pre-carbonated with either air or waste $CO_2$ prior to discharge into the ocean. The direct measurement of dissolved inorganic carbon concentration (DIC = $[CO_{2aq}]$ + $[H_2CO_3]$ + $[HCO_3^-]$ + $[CO_3^{2-}]$) concentration added to the discharge stream (post-carbonated and air equilibrated DIC minus pre-carbonated DIC) times the discharge flow rate integrated over time allows a quantification of C captured and added to the ocean. In addition to analytical precision and accuracy, the frequency of sampling and analysis relative to the temporal variations in discharge DIC and flow rate then dictate the precision and accuracy of quantifying the carbon captured and added to the ocean. Verification then turns to the confirmation of the permanence of the ocean C storage (discussed below).

Ideally, the plume of alkaline, C-rich water added to the ocean would be continuously and perpetually monitored using high-spatial and temporal resolution measurements of DIC. However, as the plume is mixed and diluted with ambient seawater the ability to discern the added C from ambient C will become increasingly difficult. To put this into perspective typical analytical precision of seawater DIC is +/- 0.1% (Dickson et al. 2007). Thus, it would take more than 38 Gt C addition to a well-mixed global ocean before it could be reliably detected in an average sample of seawater. So, verification of ocean C must concentrate in the immediate location where C addition occurs and is detectable, and where the fate of the added C beyond the limit of detection can likely only be estimated via modeling/extrapolation or possibly via the use of proxies or tracers.

Even within the area of detection conventional seawater sampling resolution for DIC analysis will be limited by the platforms available for such sampling/measurement (e.g. ships, boats), which can be extremely expensive to operate. For this reason, it will be important to explore the use of less expensive, autonomous underwater vehicles (AUVs) or buoys to either sample seawater for later DIC analysis or preferably be equipped with sensors allowing real-time measurements (pH, $pCO_2$, alkalinity) to indirectly determine total DIC and then determine the newly added DIC portion by subtracting the total DIC from background/baseline measurements.

Loss of added DIC concentration beyond that caused by mixing and dilution with ambient seawater can be determined by the use of a passive, easily detected dye or tracer such as fluorescein or Rhodamine added to the discharge stream. Here, any concentration change that does not parallel the dilution of the tracer in the ocean will indicate a loss (or gain) of a chemical constituent by means other than dilution. Obviously, this method will be complicated/imprecise in settings where the background chemical concentrations are temporally or spatially highly variable and where sample/measurement resolution may not be adequate to fully characterize such features. Accurately determining background/baseline C chemistry variability could prove to be a significant determinant of OAE carbon tracking and verification accuracy/uncertainty.

*$CO_2$-reactive alkalinity* - Unlike verifying the CDR achieved via the addition of pre-carbonated alkalinity, uncarbonated OAE poses the additional challenge of having to quantify $CO_2$ uptake in the ocean that occurs after alkalinity addition, as well as the challenge of tracking and verifying the resulting ocean C storage. Furthermore, this alkalinity could be added in solid, undissolved form in which case particle sinking rate relative to particle dissolution rate will

affect when, where or if dissolved alkalinity is available for carbonation in the water column. As previously discussed, the depth at which dissolved alkalinity is made available for carbonation will dictate how soon atmospheric $CO_2$ is affected, with alkalinity added to surface mixed-layer waters having the most immediate atmospheric impact.

Assuming a release of $CO_2$-reactive alkalinity into a given body of surface water, the general verification and monitoring plan would be to measure seawater pH, DIC concentration, alkalinity concentration, $pCO_2$ (or any 2 of these parameters to calculate the remainder) downstream from the release to monitor the following sequence of events:

1) Elevation of seawater alkalinity concentration and pH to maximum levels above background in the immediate vicinity of alkalinity addition. In the case of solid alkalinity addition, effects on surface ocean chemistry will be delayed/attenuated as determined by the rate of solid dissolution relative to dilution and sinking.
2) Expansion in the volume OAE-effected seawater coupled with declines from alkalinity concentration and pH maxima (1) due to mixing and dilution. This is accompanied by an elevation of DIC (relative to background) caused either by the retention of $CO_2$ that would have otherwise degassed to air or the ingassing of $CO_2$ from the atmosphere.
3) Continued expansion of affected water volume and OAE-effected CDR, with corresponding chemical concentrations declining to background levels as alkalinity is mixed and diluted with ambient seawater.

The net effect will be for the added, $CO_2$-reactive alkalinity and resulting $CO_2$ undersaturation to spread, affecting an expanding ocean area as mixing and dilution occurs, but where CDR will become increasingly difficult to directly detect as mixing and dilution causes the chemical signals of OAE to decline into background levels and thus become undetectable. Illustrations of these concepts are shown in Figures 3-7.

*Longevity of alkaline C storage* - Once bicarbonate and carbonate ions are added to seawater via either the addition of $CO_2$-reactive or pre-carbonated alkalinity to the ocean, what then is the expected lifetime of that $CO_2$ sequestration? On empirical grounds, assuming that i) riverine input is the only source of seawater alkalinity, ii) $CaCO_3$ precipitation and burial in sediments represents the only seawater alkalinity sink, and iii) this system is in steady state (inputs = outputs), then the 0.3 Gt C/yr entering the ocean as riverine alkalinity relative to the 37,800 Gt of alkaline C residing in the ocean, then implies a mean residence time of carbonaceous seawater alkalinity of about 100,000 yrs (Middelburg et al. 2020). An even longer mean residence time of 1 Myrs can be inferred from the longevity of $Ca^{2+}$ in seawater, whose seawater life cycle should closely parallel that of alkalinity.

The preceding provides some assurance that once added to seawater, carbonaceous alkalinity will indeed be very long lived. Nevertheless, additional direct evidence of this may be desired/required by credit markets, especially under oceanographic conditions where there may be an increased risk of alkalinity loss due to biotic or abiotic calcification via reversal of rctn. 4: $Ca^{2+} + 2HCO_3^- \text{--->} CaCO_{3s} + H_2O + CO_{2g}$. Yet such marine calcification and carbonate burial globally only amounts to about 1 Gt C/yr (Middelberg et al. 2020), or less than 0.003% of resident seawater alkaline C. The calcification reaction converts half of the C originally contained in seawater bicarbonate ions into very long lived $CaCO_{3s}$ and liberates the other half as unsequestered $CO_2$. The longevity of C sequestration is greatly increased by the formation of $CaCO_{3s}$. However, the penalty here is that an immediate atmospheric $CO_2$ source in created with half of the previously stored seawater bicarbonate being converted to dissolved $CO_2$ that would at least temporarily acidify the seawater before ultimately being released to the atmosphere. A special caveat here is that if the seawater bicarbonate originated from the dissolution of $CaCO_{3s}$ (rctn. 4 above), then subsequent precipitation of $CaCO_3$ would negate any C sequestration, via the reversal of rctn. 4.

## 4) Further MRV Specifics (Outline)

Discussion of MRV strategies in light of the preceding and how to tailor to specific oceanographic site/conditions, types of alkalinity and discharge methods.

*Modeling* - Discuss the need for modeling to extrapolate beyond direct measurements and to predict ultimate fate and effects of OAE. Use of lab and field experiments at specific sites to inform, refine and verify models.

*Net CDR* - As previously stated, any $CO_2$ removal, emissions reduction and /or C storage occurring in the ocean via OAE will require a full LCA of $CO_2$ emissions associated with a specific OAE application in order to determine the net CDR achieved. Details of LCA methods...

*Monitoring and assurance of environmental safety* - Laboratory and field testing and evaluation of chemical and biological responses to a given OAE - how and where. Predictive modeling of chemical and biological responses to OAE, and verification of responses via field testing and monitoring (Modeling above). Details....

*Analytical methods* - Details of analytical methods for pH, DIC, alkalinity, $pCO_2$, etc. (citing Dickson et al. 2007 and others) including discussion of sampling, measurement and sensors, and associated precision, accuracy, and implications for CDR measurement limitations……

*Seawater chemistry baseline* - Discussion of the importance of background/baseline seawater measurements, spatial/temporal variations, and implications for discerning an OAE signal from background/baseline chemistry "noise"......

*Tracers/proxies* - Discussion of the use of passive tracers to separate dilution effects from other factors affecting alkalized water chemistry/biology……. Could the measurement of other/additional seawater chemistry parameters ($^{13}C/^{12}C$, metal ion isotopes, etc.) allow for OAE CDR MRV beyond that possible using conventional pH, DIC, alkalinity and $pCO_2$?

*Additional Topics* - Including and incorporating social and legal dimensions in developing MRV, mechanisms for refining MRV as R&D and new information become available, changes required in MRV as OAE scales to larger capacities and/or involves multinational participation, etc.

## 5) Illustration of Possible Seawater Chemistry Responses

The following figures are conceptual models of seawater chemistry response to $CO_2$-reactive alkalinity addition to the ocean as a function of time or distance from discharge. All responses here are assumed to initially rise significantly above detection limits as dictated by analytical precision and by variability of background seawater chemistry.

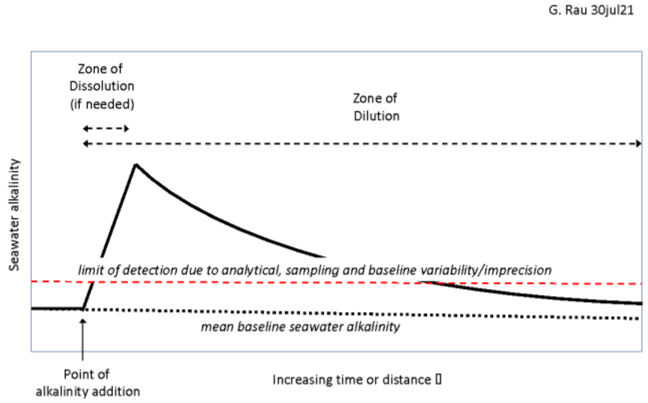


Figure 3. Seawater alkalinity concentration initially peaks and then declines as a function of time/distance from discharge, due to mixing and dilution with ambient seawater. Alkalinity maximum will be delayed/attenuated if the alkalinity is initially added as a solid and dissolves at some finite rate. The alkalinity signal eventually drops below level of detection due to dilution (Fig. 6)..

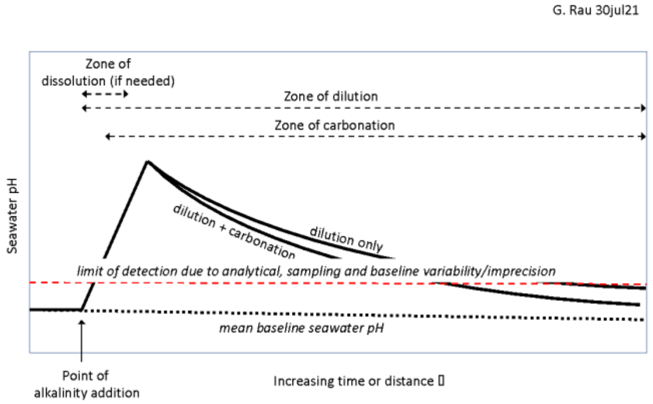


Figure 4. Conceptual sequence of OAE-affected pH, also showing the effect of the carbonation of the alkalinity with seawater $CO_2$ and the invasion of air $CO_2$ (Fig. 5).

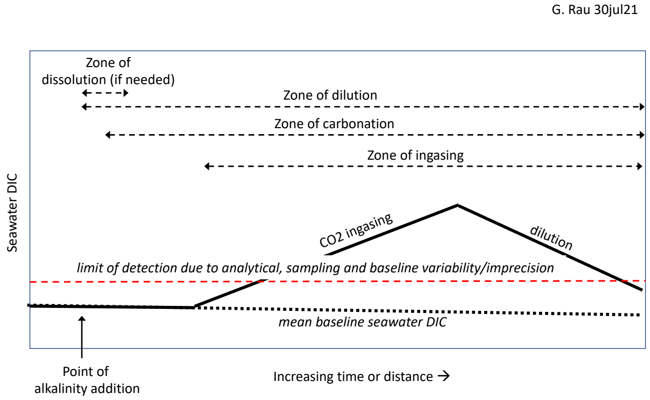


Figure 5. Increase in DIC relative to background resulting from the ingassing of atmospheric $CO_2$. Integration of this measurement over time and space allows for a calculation of total CDR effected (Fig. 7).

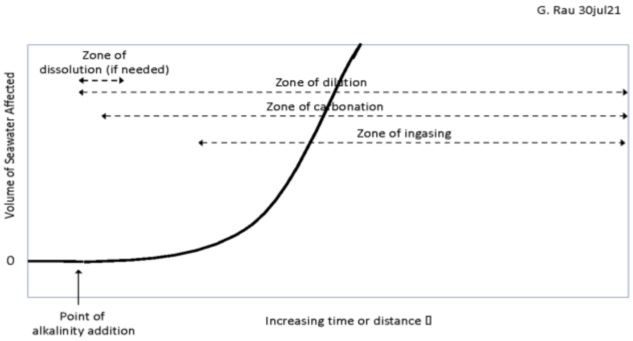


Figure 6. Possible volume of surface seawater affected by OAE vs time or distance.

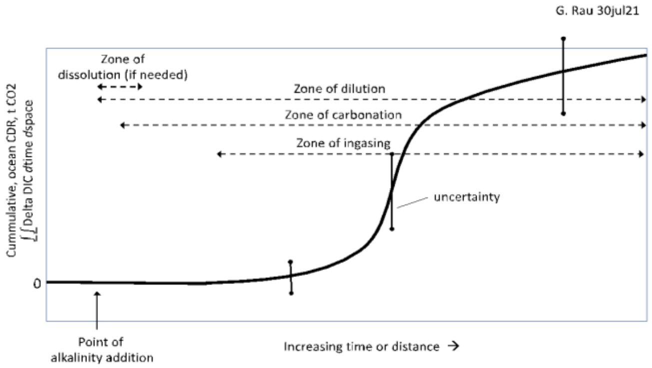


Figure 7. Cumulative DIC increase per unit seawater volume (Fig. 5) combined with the volume of seawater affected (Fig. 6) to yield a measure of total CDR by the OAE (+/-uncertainty) as a function of distance/time.

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