

**Measurement, Reporting, and Verification (MRV) Protocol for OAE mCDR by mineral addition (V3.0)**

**October 2023**

**Version history**

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| **Revision** | **Date** | **Description** |
| [Version 1.0](https://github.com/Planetary-Technologies/MRV/releases/tag/v1.0) | August 12th, 2022 | Completed and agreed upon by Planetary and Shopify in advance of Planetary’s initial methods test conducted in September 2022. |
| [Version 2.0](https://github.com/Planetary-Technologies/MRV/releases/tag/v2.0) | February 23rd, 2023 | Updated to incorporate results from continued laboratory experimentation, learnings from a 3-day methods test conducted in the UK in September 2022, and advancing the emissions accounting aspect of the protocol. |
| Version 3.0 | Revised draft following Isometric review October, 2023 | Updated following extensive external comments and suggestions in response to Version 2, notably including uncertainty analysis, and in accordance with ISO 14064-2. |

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# Background

This document is a working draft of Planetary’s approach to the Measurement, Reporting, and Verification (MRV) of carbon dioxide removal (CDR) via ocean alkalinity enhancement by mineral addition, and builds on earlier Versions 1 and 2. Insofar as they apply to this protocol, the current version has been prepared in accordance with the requirements of ISO 14064-2. The document will be periodically refined and improved as both Planetary and the global ocean community learns through continued research and experimentation in the laboratory and in the field. Comments or suggestions for improvement are most welcome and can be posted at <https://github.com/Planetary-Technologies/MRV> or sent at any time to PlanetaryMRVFeedback@planetarytech.com.

A robust MRV protocol, agreed to by provider, verifier, and customer, and supported by ocean science, is essential in order to ensure that greenhouse gas removals are appropriately quantified, monitored, accounted for, and permanently retired.

## Introduction to OAE

The ocean contains an estimated 39,000 billion tonnes of carbon (GtC), around 10 times greater that the terrestrial carbon inventory and 50 times that of the atmosphere, and is playing an important role in mitigating climate change, having taken up about one third (660 GtCO2 ± 20%) of fossil fuel CO2 emissions during the industrial era[[1]](#footnote-1). CO2 is a minor component of Earth’s atmosphere because of its transformation into carbonate rocks and ocean alkalinity as a result of surface mineral weathering on a geological timescale[[2]](#footnote-2). Similarly, the ocean will be the natural long-term sink of all anthropogenic CO2 emissions, on a timescale of at least 100 kyr, as a result of the action of processes such as the ocean solubility pump, reaction with carbonate sediments, and the surface run-off of bicarbonate from the terrestrial weathering of silicate rocks[[3]](#footnote-3). Given this immense inventory and its continuing role as a major natural sink for atmospheric CO2, the enhancement of natural processes to accelerate the atmosphere-ocean transfer of CO2 promises to be an important carbon dioxide removal (CDR) option.

The addition of alkalinity to the ocean—a process termed ocean alkalinity enhancement (OAE)—can achieve this acceleration. Planetary’s current OAE approach involves the addition of fine magnesium hydroxide particles (Mg(OH)2; henceforth MH), in slurry form, to wastewater, or other industrial outfalls that discharge into the ocean. As MH is a CO2-reactive form of alkalinity, its addition to water results in the simultaneous increase in pH, and the conversion of dissolved CO2 into bicarbonate and carbonate ions (See Box 1).

The fundamental chemistry of this reaction in the ocean is illustrated in Figure 1. The resulting reduction in the partial pressure of CO2 (pCO2)in seawater either:

1. under saturates the seawater in CO2 relative to air, thus forcing a CO2 flux from the air to the ocean, or
2. in waters that are supersaturated in CO2 (such as ocean upwelling areas or around wastewater outfalls), lowers the water’s pCO2 such that loss of CO2 to air is reduced or avoided.

OAE CDR is thus achieved either by chemically enhancing the ingassing of CO2 from air to ocean or by reducing CO2 outgassing to the air. In either case, CO2 is securely stored in the ocean while alkalinity, carbon content, and pH are raised relative to ambient conditions.

***Box 1: The ocean carbonate system***

When CO2 dissolves in seawater it will either remain in a dissolved form (CO2(aq)) or be hydrated to form carbonic acid;

CO2(aq) + H2O ↔ H2CO3 B1.1

Under seawater conditions in excess of 99% is in the form CO2(aq), the sum of CO2(aq) plus H2CO3 being conventionally denoted as H2CO3\*. Dissolved CO2 can then react with hydroxy ions (OH-) according to the reactions;

CO2(aq) + OH¯ ↔ HCO3¯ B1.2

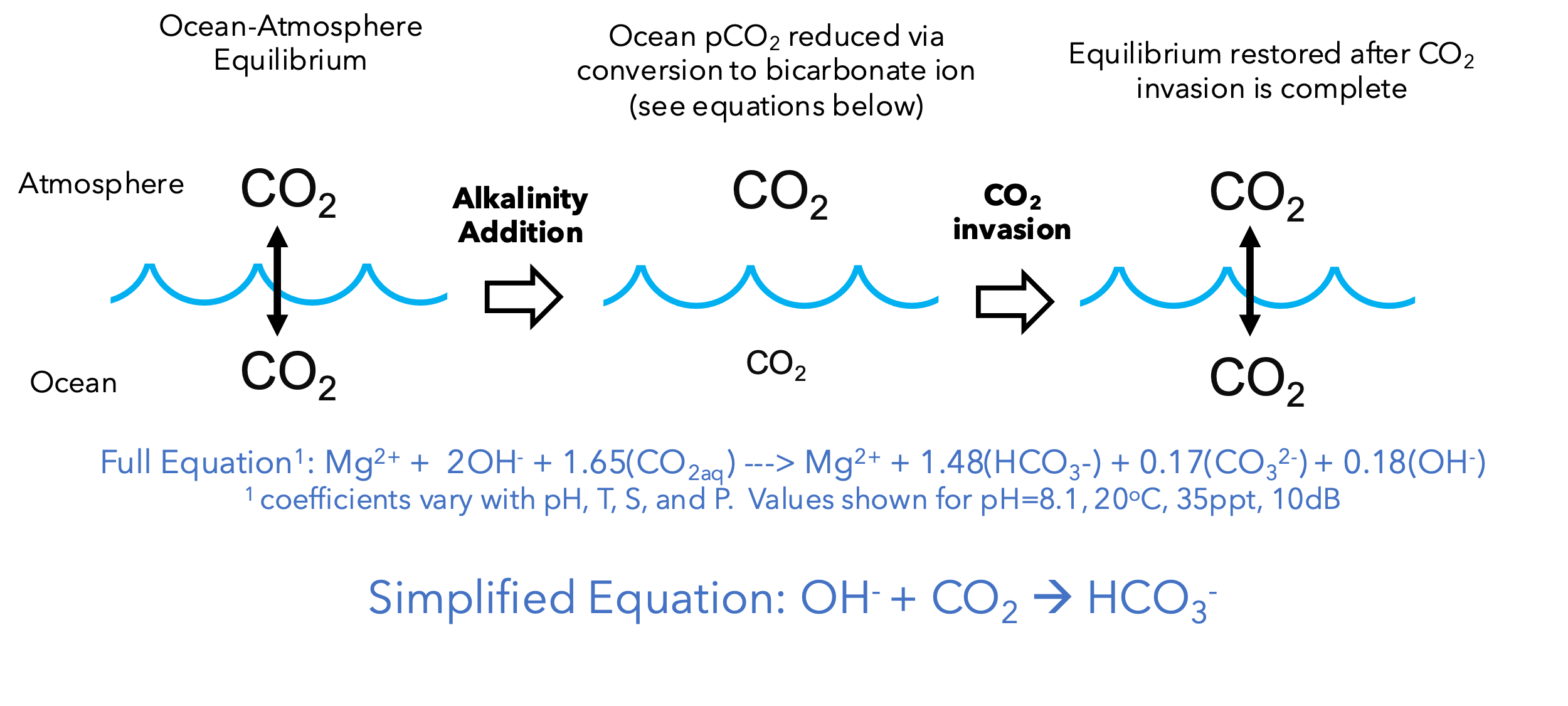
HCO3¯ + OH¯ ↔ CO32- + H2O B1.3

These reversible reactions are driven to the left or right depending on the seawater pH, and the equilibrium partitioning between H2CO3\*, HCO3¯, and CO32- (which together make up the total dissolved organic carbon, or DIC) is illustrated in the Bjerrum plot below.

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Under current seawater conditions, with pH ~8.05, an increase in pH resulting from alkalinity addition will reduce the dissolved CO2 concentration [CO2(aq)] by driving reactions B1.2 and B1.3 to the right. The related drop in CO2 partial pressure (pCO2) will then drive air-sea gas exchange, effecting CDR as the pCO2 equilibrium is restored.



**Figure 1.** Basic chemistry of OAE by MH addition

Various site-specific inefficiencies and uncertainties—discussed in Appendix 1—need to be accounted for in order to derive the CO2 removal effected for a given quantity of added alkalinity, while CO2 emissions associated with Planetary’s end-to-end OAE process, determined by Life Cycle Analysis (LCA), also need to be subtracted to determine net CDR.

In the case of municipal wastewater, the intense microbial respiration taking place in the treatment process, fuelled by waste organic matter, means that these discharges are very highly supersaturated in CO2 relative to air. Thus, by adding alkalinity to these streams there is significant potential for initial CO2 removal to occur in the pipe before the alkalized wastewater is delivered to the ocean. This provides an opportunity to directly demonstrate the immediate reduction in pCO2 following alkalinity addition.

# Determination of net CDR

CO2 is the only greenhouse gas (GHG) removed as a result of OAE, and this section describes the methodology for determining net removals. Project related life-cycle emissions, both of CO2 and others GHGs, are discussed in Section 2.

## The ocean baseline scenario

The relevant baseline for determining the net CDR impact of OAE is the quantity of dissolved inorganic carbon (DIC)—primarily as bicarbonate and carbonate ions—present in the ocean interior, where it remains out of contact with the atmosphere for all climate relevant timescales. This DIC inventory is currently increasing at a rate of ~ 3 GtC/yr as a result of the drawdown of CO2 emissions from fossil fuel combustion and land-use change1, and its future evolution will depend on the future trajectory of these emissions, as well as on the progress of marine CDR (mCDR) activities, including OAE. The GHG sources, sinks and reservoirs (SSRs) relevant to the OAE methodology—both for the baseline scenario and for quantifying carbon removals—are therefore the atmospheric and oceanic carbon reservoirs and the air-sea CO2 flux (SOCEAN in the terminology of the annual carbon budget1).

The CDR quantification methodology described here is based on the retrospective validation of numerical models against actual conditions in the atmosphere and ocean. At project level, the baseline scenario is therefore the regional air-sea CO2 flux evaluated using such models over the project period but in the absence of the project. At scale, when an ocean “signal” is detectable over a representative area, model validation will incorporate measurements of the full suite of carbonate system parameters (DIC, pH, pCO2, TA), with changes in the bicarbonate and carbonate concentration calculated using well established seawater chemistry[[4]](#footnote-4).

This methodology does not make any assumption regarding future emissions and their impact on the ocean. The long-term emissions trajectory, and particularly its impact on ocean acidification, is relevant when considering the potential biocalcification response to OAE, and this is discussed further in Section 2.4.4.

## Determining CDR – gross, net removed, and creditable

As illustrated in Figure 1, the gross quantity of dissolved CO2 (CO2aq) that is removed from seawater and converted to bicarbonate (HCO3¯) and carbonate (CO32-) ions is determined by the stoichiometric molar ratio between CO2 consumed and MH added. This ratio is shown in the figure as 1.65 moles CO2/mole MH. Given that CDR crediting is measured in tonnes CO2, the mass equivalent of the preceding ratio is used (in this case, 1.25 tCO2/tMH) and is termed “CDR/MH” (or ‘CDR/ALK’ more generally)[[5]](#footnote-5). It is important to keep in mind that this ratio varies with the pH, temperature (T) and salinity (S) attained following dilution in the ocean (see Box 2 and Appendix 1). The maximum theoretical CDR achievable by alkalinity addition can be calculated by applying this ratio to the mass of alkaline material added;

**CDRMAX**= ALK x CDR/ALK (1)

where ALK is the tonnes of CO2-reactive alkaline material added to seawater and CDR/ALK is the maximum tonnes of CDR possible per tonne ALK addition. This ratio is derived from knowledge of the CDR/ALK molar ratio for a given seawater chemistry state (Box 2) and converted to units of tonnes CO2 drawdown/tonne ALK addition through knowledge of the mol weights of CO2 and the alkaline material being used. For example, if the alkalinity is Mg(OH)2 (MH), then the molar CDR/ALK ratio (e.g., 0.825) must be multiplied by the ratio 44 g per mol CO2/58.3 g per mol MH, and then multiplied by the mols of alkalinity per mol MH (=2) to yield a mass ratio of 1.25 tonnes CO2 drawdown/tonne MH addition.

ALK is determined from the concentration of mineral present in the slurry multiplied by the volume of slurry added to the outfall. The rate and duration of slurry dosing are closely monitored (see Section 4.1), and the chemical conditions in the receiving ocean waters are measured, including an assessment of background variability across different timescales (daily, seasonally), to determine an appropriate CDR/ALK ratio for the initial calculation of CDRMAX. This CDRMAX value is termed “initial” because the CO2 removed will ultimately be determined by the CDR/ALK calculation in the 3D model, which is in turn determined by the modeled ocean properties at the point (x,y,t) of air-sea gas exchange.

From the maximum CDR calculated in this way, the CO2 removed from the atmosphere—or prevented from escaping to the atmosphere—(CDRGROSS) is calculated as;

**CDRGROSS** = CDRMAX x η (2)

where ηrefers to CDR efficiency or the fraction of CDRMAX that is actually achieved in the ocean[[6]](#footnote-6). This efficiency embodies the two main factors influencing CDR efficiency;

1. if the alkalinity is in solid form, the fraction of the added alkalinity that dissolves in “surface waters”, and
2. the fraction of the resulting alkalized, pCO2-depleted water that remains in these “surface waters” until pCO2 equilibrium between air and seawater is restored.

Simplistically, “surface waters” means the upper mixed layer of the ocean, but since the mixed layer depth (MLD) is dynamic on daily to annual timescales, the broader term “surface waters” is used here to denote waters that can be brought into the mixed layer on some future climate relevant timescale. For example, particle dissolution below a shallow—summer stratified—MLD can be brought back into contact with the ocean surface as a result of the autumn MLD deepening, or pCO2-depleted water that is subducted below the winter MLD may be brought back into contact with the surface through advection to shallower water depths by deeper currents.

Direct measurement of CDRGROSS would require the frequent measurement of air-sea CO2 flux over a wide ocean area, and the quantification of the OAE “signal” on top of a highly variable background. It is widely recognized that this is not currently feasible[[7]](#footnote-7),[[8]](#footnote-8), and the approach adopted here (further discussed in Appendix 1) relies on numerical modeling to assess η and hence CDRGROSS. Improving our ability to measure this type of efficiency more directly remains a priority across many CDR approaches, and some possible avenues towards this goal for OAE are briefly outlined in Section 7.

***Box 2: Determining an initial CDRMAX***

The stoichiometric ratio determining the maximum increase in DIC following alkalization depends on the T, S, and pH of seawater at final pCO2 equilibration – before the parcel of water departs from contact with the ocean surface.

This dependence is illustrated in the following figures, and can be expressed as;

CDRMAX (Delta DIC/Delta TA) = 2.8982 - 0.0031 \* S - 0.2319 \* pH - 0.0044 \* T

for an equilibration pCO2 of 420 µatms, where T is in °C, S is in ppt, and using the seawater pH scale.

Alternative expressions for different equilibration pCO2 values, or different pH scales can be readily derived using online multiple linear regression tools[[9]](#footnote-9).

The molar CDR/ALK ratio can be converted to a mass ratio (tonnes CO2 drawdown/tonne ALK addition, or simply tonnes/tonne) by multiplying the molar ratio by 44 g per mol CO2/g per mol of the specific alkaline material added, and then multiplying by the mols of alkalinity per mol of the specific alkaline material. For example, the mol wt of Mg(OH)2 is 58.3 and the mols alkalinity per mole of Mg(OH)2 is 2. The resulting mass ratio in grams/gram is the same for tonnes/tonne.

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In V2 of this protocol, a 1-year time horizon was indicated for η, however, further modeling studies have indicated that this would not be appropriate for most sites. As discussed in Appendix 1, site-specific time horizons for η will be used, with an absolute cut-off at 10-years after alkalinity addition.

To determine the net quantity of CO2 removed, allowance must then be made for the emissions incurred by the OAE intervention. Thus;

**CDRNET** = CDRGROSS - ELCA (3)

where ELCA is the tonnes of CO2e (CO2 equivalents) emitted as a result of the production, transportation, and distribution of the total mass of alkaline material used in the operation, and emissions from other project activities, as well as (ultimately) an allocation of corporate “overhead” emissions. The emissions accounting methodology is further discussed in Section 3.

CDRNET as determined by Equation (3) is subject to a number of uncertainties (discussed below) and the issuance of a removal credit requires a high confidence that the actual quantity removed will exceed the quantity credited. A discount, or holdback is therefore applied to arrive at this high confidence creditable quantity;

**CDRCRED** = CDRNET - CDRHBACK (4)

where CDRHBACK is a CO2 quantity, determined from uncertainty analysis of CDRNET (see below), that is withheld from initial crediting but may become creditable as uncertainties are reduced. For example, this might be as a result of the establishment of a firm supply chain for alkalinity production and distribution, with well constrained LCA emissions, or the history matching[[10]](#footnote-10) of the ocean model to the actual climatology during the period from alkalinity addition to full air-sea equilibration.

Combining Equations (1) to (4) gives;

**CDRCRED** = ALK x CDR/ALK x η - ELCA - CDRHBACK (5)

Equation (5) represents Planetary’s fundamental approach to calculating CDRCRED.

As noted above, at sites where alkalinity is added to CO2-supersaturated wastewater prior to its discharge, CO2 removal will start within the wastewater pipe, presenting an opportunity to clearly demonstrate the impact of alkalinity addition on the CO2-bicarbonate-carbonate balance (see Section 1) . This in-pipe removal was demonstrated in Planetary’s first wastewater monitoring test, at Hayle in Cornwall, during September 2022, as shown in Figure 2. Such measurements confirm the in-pipe impact of alkalinity addition on biogenic CO2, as well as compliance with in-pipe permit regulations and, in combination with in-pipe chemical modeling, can provide assurance that there are no concerns for the pipe infrastructure, for example due to precipitation.

However, crediting of such uptake remains subject to the CDR efficiency term, η, where the fraction of the removed carbon that would otherwise have degassed to air will be reflected (quantifying the additionality of the wastewater CDR). This, plus the fact that the ultimate CDRGROSS will be determined by the chemistry of the diluting seawater via the CDR/ALK term (Box 2), means that a direct measurement of CDR in the wastewater cannot be readily incorporated into the CDR calculation summarized in Equation (5). For these reasons the CDR that occurs upstream of ocean discharge is not considered further.

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**Figure 2**. %CO2 differences in a wastewater pipe measured upstream (blue) and downstream (red) of MH addition. Black horizontal lines indicate the periods of MH addition during the 3-day test. pCO2 is approximately equal to % CO2 x 1000 μatm/% at 1 atmosphere (atm) total pressure[[11]](#footnote-11).

## Analysis of uncertainties in determining CDR

The main uncertainties affecting the determination of CDRNET are summarised in the following table, and discussed below.

|  |  |
| --- | --- |
| **Factor determining CDRNET** | **Key uncertainties** |
| ALK; quantity of MH added | MH slurry density, rate, and dosing duration.  Composition (%MH) of raw ALK product |
| CDR/ALK; stoichiometric ratio (ΔDIC/ΔTA) | Ocean conditions (T, S, pH) at the location of air-sea equilibration |
| η; model CDR efficiency | Ocean conditions (T, S, pH) at the location of air-sea equilibration; loss of pCO2 depleted water from the ocean mixed layer and of undissolved ALK particles (depending on dissolution rate). |
| ELCA; life cycle embedded CO2e emissions | Transportation modes, distances and carbon intensities; mining and comminution emissions; direct and allocated project and corporate emissions |

Equation (3) provides the basis for determining a mid-case estimate of CDRNET, the net CO2 removed as a result of the dispersal of a given quantity of alkaline material. Each term in, or implicit in, the equation (i.e., ALK, CDRMAX, η, and ELCA) is subject to a range of uncertainties, and the identification, quantification, and combination of these uncertainties allows the determination of a probability density function (pdf) for CDRNET. This distribution can then be used to determine a discount (i.e., CDRHBACK) that reduces the mid-case CDRNET to a high confidence quantity suitable for crediting, for example with a 95% probability of exceedance.

Among the main sources of uncertainty in CDRNET will be the potential for sinking of undissolved particles and subduction of alkalized seawater (affecting η), and uncertainties in the carbon intensity of transportation modes in the alkalinity supply chain (affecting ELCA). A comprehensive list for each factor in Equation (3) is given in Section 4.

In most cases the individual uncertainties will be symmetric, and can be combined using the simple variance summation approach (see Box 3). Where uncertainties are not symmetric, analytical approaches are complex and it is common practice to use Monte Carlo simulation (Box 4).

**Box 3: Error propagation**

If the uncertainties in quantities B and C are subject to normal (Gaussian) distributions, the uncertainty in the combinations B+C, B-C, B/C can be calculated using the standard error propagation formulae;

For A = B + C or B – C;

σ2A = σ2B + σ2C , so that σA = (σ2B + σ2C)1/2

where σX is the standard deviation and σ2X is the variance of (assumed Gaussian) probability distribution for quantity X.

For A = B/C;

(σA/A)2 = (σB/B)2 + (σC/C)2, so that σ2A = A2 ((σB/B)2 + (σC/C)2)1/2

Figure 3 illustrates the variance summation approach to determining CDRHBACK. The rightmost (blue) curve shows the cumulative probability distribution for the quantity of alkalinity added. For MH as the alkalinity source this is 2 x tonnes MH. Next, to the left, is the equivalent curve for CDRMAX (orange), where uncertainties in ALK and CDR/ALK terms have been combined. Note that the orange curve has shifted left according to the CDR/ALK ratio of 0.825. Next is the CDRGROSS cumulative probability curve (grey), including uncertainties in η, and last is the CDRNET curve (gold), including uncertainties in ELCA. CDRCRED can then be read from the CDRNET curve at the required probability of exceedance (shown here as 95%), and CDRHBACK is the difference between this high confidence number and the calculated mid-case CDRNET. Note that the mid-case value will have a 50% probability of exceedance if all uncertainties are symmetrical.

In this example, for 5 tonnes MH added, the calculated CDRNET is 7.15 tonnes CO2, and, given the accumulated uncertainties, the point along the x-axis where this CDRNET reaches the 95% exceedance probability (i.e., the CDRNET (P95) or CDRCRED) is 6.15 tonnes, giving a CDRHBACK of 1.0 tonnes CO2.

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**Figure 3;** Variance summation approach to CDRHBACK determination

**Box 4: Monte Carlo simulation**

Monte Carlo methods are a class of computational methods that use random sampling to solve mathematical problems[[12]](#footnote-12).

In the present context, the repeated random sampling approach can be used to combine uncertainties that cannot be treated with sufficient accuracy by the simple algebraic approach described in Box 3, for example due to their being highly skewed.

A Monte Carlo approach to assessing the uncertainty in a quantity A, where;

A = B x C – D

involves the sampling of B, C, and D from their respective probability distributions, calculation of the resulting A’s, and construction of the probability density function (pdf) of A by repeated sampling of B, C, and D.

Unlike the algebraic approach outlined in Box 3, a Monte Carlo simulation will produce a pdf of A that more adequately reflects any asymmetry in the pdfs of the inputs B, C, and D.

## Planetary’s Ocean Carbon Calculator

The outfall characteristics, oceanographic conditions, and numerical models appropriate and available will vary at each project site. As a result, the finer details of the modeling approach to ultimately calculate CDRNET and CDRCRED, will change accordingly. Rather than pre-selecting models and approaches, this protocol makes use of Planetary’s Ocean Carbon Calculator tool. This tool selects and runs appropriate models for the site, returning a calculated value for η and its uncertainty, along with a crediting schedule based on the progression of air-sea flux re-equilibration. The tool provides full accountability and transparency to verifiers and is based on the best available models for the site.

## Additionality, permanence, and reversal risks

This section briefly discusses some key uncertainties and potential risk areas related to CDR via OAE, several of which have been highlighted in recent academic peer-reviewed publications[[13]](#footnote-13), and in the CarbonPlan Verification Framework pathway for the OAE by mineral addition.[[14]](#footnote-14),[[15]](#footnote-15)

### Additionality of CDR by OAE

The project activities supported by this protocol are entirely reliant on the availability of financing for carbon removal credits. This funding incentive is what ultimately drives the development and initial deployment of OAE projects and the resulting CDR, thus inherently making the activity additional. The counterfactual would be the non-use or disposal of the alkaline material.

Researchers have raised the possibility that certain OAE approaches could impact natural systems in such a way that complicates the additionality concept described above.[[16]](#footnote-16) For example, experiments of alkaline materials added to beach sands have been shown to reduce rates of calcium carbonate dissolution within sediments that would otherwise naturally release alkalinity into the water column. This case only applies to OAE techniques that result in deposition of alkalinity on the seabed, and raises further questions regarding other benthic reactions that produce and consume alkalinity (e.g. sulphate reduction). Nevertheless, this highlights the importance of monitoring seafloor interactions within OAE projects (see section 4 and appendix 2), the important role academic research plays in advancing OAE and CDR, and the need for companies to ‘follow the science’, which is core to Planetary’s Science and Technology Code of Conduct.

### Permanence and reversal risks

A number of risks related to CDR permanence and reversal are summarised in the following table, and discussed below.

|  |  |
| --- | --- |
| **Permanence risk** | **Description** |
| Atmospheric pCO2 reduced below pCO2 in the surface ocean | Requires very effective global emissions reduction and CDR; could be countered with additional OAE. |
| Seawater advection to lower CDR efficiency conditions prior to long-term subduction | Small effect that will be assessed by project models; a focus area of ongoing research |
| **Reversal risk** | **Description** |
| Ocean carbon cycle; CaCO3 precipitation | Steady state annual alkaline C loss rate of 0.00009%/yr giving a 105 yr mean lifespan of alkaline C in the ocean |

The mean residence time in the ocean of alkaline dissolved carbon (alkaline C) i.e., bicarbonate and carbonate ions, charged-balanced by cations other than H+, is about 105 yrs17. Following the increase in alkaline C as a result of hydroxide addition, via the reaction shown in Figure 1;

Mg2+ + 2OH¯ + 1.65 CO2(aq) → Mg2+ + 1.48 HCO3¯ + 0.17 CO32¯ + 0.18 OH¯

the main potential loss mechanism is via biotic and possibly some abiotic CaCO3 precipitation via the reaction;

Ca2+ + 2HCO3¯ → CO2(g) + CaCO3(s) + H2O. (7)

Based on the annual global input of alkaline C from rivers (0.3 GtC/yr), the pool of dissolved bicarbonate and carbonate alkalinity resident in the ocean (about 34,000 GtC)[[17]](#footnote-17), and assuming a steady state, an annual alkaline C loss rate of 0.00009%/yr can be calculated. The assumption of steady state seems valid for near-term carbon additions to the ocean that will be tiny relative to the global resident C and considering the rapid dilution of the alkaline C added that returns seawater chemistry essentially to ambient levels. We therefore assume that the lifetime of added alkaline C will be the same as that of present alkaline C in the ocean. Over its 105 yr mean lifespan, about half of the alkaline C is eventually lost from seawater as CO2 (returning to the atmosphere) and the remainder precipitates as CaCO3(s) to ocean sediments (Reaction (7)), where it joins the multimillion-year geologic C cycle.

A second way that seawater alkaline C can be returned to the atmosphere is if the pCO2 of the overlying atmosphere were to be reduced below the pCO2 in the surface ocean, e.g., as a result of very effective global emissions reduction and CDR. In this case surface ocean CO2 would tend to escape to the atmosphere in order to equalize air/sea CO2 partial pressures. This ocean “rebound” is well studied[[18]](#footnote-18),[[19]](#footnote-19). Such loss of CO2 from the ocean surface would, through chemical equilibria, force the loss of carbon among both alkaline and non-alkaline dissolved inorganic C constituents in seawater that, if large enough, could be directly measured as a loss of global mean sea surface DIC and an elevation in seawater pH. In theory this loss of DIC could be countered by performing additional OAE CDR, though this would further elevate seawater pH.

More relevant to nearer-term OAE deployment is the potential for CDRGROSS to either increase or decrease as a result of seawater advection following initial air-sea equilibration up until its eventual subduction. For example, if equilibrated seawater advects to a lower (higher) temperature region and is re-equilibrated before subduction, CDRGROSS would increase (decrease) by ~0.5%/°C. Alternatively, if the total alkalinity (TA) and salinity (S) of equilibrated seawater are reduced (increased) as a result of mixing with seawater having a higher (lower) freshwater content, then re-equilibrated would increase (decrease) CDRGROSS by ~1.5% per 10% change in TA and S. The net effect of such changes is likely to be small in most cases, and will be assessed in project models, although quantification will be subject to higher uncertainties due to the long timescale involved. The long term fate of alkalized seawater remains an active area of research in the ocean modeling community.

### Secondary precipitation risk

Alongside the potential loss of alkalinity from particle sinking and alkalized water subduction (noted above and discussed further in Appendix 1), the possibility of runaway precipitation of CaCO3 from seawater[[20]](#footnote-20) following alkalinity addition has been identified as a further potential risk to the effectiveness of OAE.

However, the reported bottle or beaker experiments[[21]](#footnote-21),[[22]](#footnote-22) do not account for the rapid dilution of alkalinity once added to wastewater and especially once entering the ocean. Based on these reported results as well as Planetary’s in-house experiments, it is certainly possible to add alkalinity to seawater in quantities that stay below, or—by dilution and dispersion—are rapidly brought below the precipitation threshold. Even for large rates of addition, dilution (in this case in a ship’s wake) has been shown to drop the concentration of alkalinity in seawater below precipitation thresholds at a rate far faster than the rate at which CaCO3 precipitation can proceed[[23]](#footnote-23).

This is especially the case for MH, which dissolves (and thus releases alkalinity) slowly, providing an additional layer of safety with respect to staying below marine chemical (and biological) thresholds. Overall, a relatively slow-release alkalinity source and a highly dilutive environment combine to greatly minimize the risk of secondary precipitation for the OAE process described here.

However, these mitigating conditions may be insufficient to eliminate the risk when the process is implemented at large scale. If discharge modelling indicates that conditions in the near-field might approach those under which secondary precipitation might be initiated, more intensive in-situ monitoring of seawater chemistry (pH, TA, and saturation state across the full range of seasonal variability) will be implemented to establish a dosing level limit to ensure secondary precipitation is avoided under all operating conditions.

### Biocalcification impact

The precipitation of calcium carbonate by calcifying plankton has been identified as a factor that could reduce the effectiveness of OAE8,[[24]](#footnote-24). Biocalcification impacts and is impacted by the ocean carbon cycle in several ways[[25]](#footnote-25);

i) it releases CO2 via Reaction (7),

ii) by consuming alkalinity it reduces the ocean’s ability to absorb CO2,

iii) it increases the availability of particulate inorganic carbon (PIC) that, by ballasting particulate organic carbon (POC) increases the efficiency of the organic carbon pump, and

iv) it is enhanced by CO2 fertilization in some ocean regions but inhibited by acidification in others.

A decline in the biotic release of CO2 (Equation (7)) results in a negative feedback on climate change, and the concern regarding OAE effectiveness arises from the potential reversal of this feedback as a result of ocean pH restoration. However, modeling studies have shown an even stronger positive climate feedback from reduced POC ballasting[[26]](#footnote-26), and there remains a lack of consensus on the magnitude—and indeed the sign—of the net effect[[27]](#footnote-27).

As discussed in Section 4, the perturbation of seawater properties resulting from OAE by MH addition will not be measurable beyond a few meters from the discharge location until deployed at a significant scale, and these effects (whether positive or negative) are therefore not relevant at the current scale of field trials.

Pending the outcome of continuing research in this area, which includes the potential for satellite-based monitoring,[[28]](#footnote-28) no allowance for a biocalcification response to OAE activities is included in this methodology. The possible need to monitor for a biocalcification response will be reviewed based on the latest research findings once field trials or early deployment reaches a scale that is expected to result in a perturbation of seawater properties that is significant when compared to local background variability.

# Emissions accounting methodology

**Box 5: Life Cycle Assessment Vs. Emissions Accounting**

Life Cycle Assessment (LCA) and emissions accounting are study methods related to the impact categories under review. Both methods will follow the subject through its lifecycle from raw material extraction, manufacturing , distribution, use, and disposal. However, the emissions accounting method is related to the climate change impacts from the discharge of greenhouse gasses. These are typically reported as CO2 equivalents (CO2e).

Meanwhile, the LCA will take into account more impact categories such as land use change, water and resource depletion. For the purpose of measuring, verifying and creating a standard reporting structure, Planetary is stating its method for developing a project emissions report.

Planetary has developed this version of its protocol in reference to the International Organization for Standardization (ISO) 14064-2 *“Specification with guidance at the project level for quantification, monitoring and reporting of greenhouse gas emission reductions or removal enhancements.*

Inquiries related to the organizational level GHG inventory will be reported separately and in accordance with ISO 140641-1 (see Figure 4).

A diagram of a project

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**Figure 4;** ISO 14060 family of standards

## Establishing a baseline scenario and system boundary

As illustrated in Figure 5 below, Planetary projects begin with the identification of an existing wastewater or seawater outfall effluent system. This system is considered the “on site” location.

On site, the relevant sources, sinks, and reservoirs (SSR’s) are identified as part of the baselining activity. This includes the organizations that maintain operational control of these systems reporting for items such as its rate of discharge and energy consumption.

Off site, any activities related to the delivery of the project are accounted for in the baseline as having not generated reductions or emissions prior to the project initiation.

For the purpose of this emissions accounting, the ocean system is considered to be in steady state with no significant contribution as either a source or a sink of CO2 prior to the project being initiated.

A diagram of a process

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**Figure 5;** Baseline scenario: On site, the outfall operator is conducting business as usual, and the local ocean area is in steady state of CO2 equilibrium. Off site, no raw material or alkalinity is disturbed.

## Project emissions

The development of the project scenario is done in accordance with the ISO 14064-2 principle of “relevance”. Project components determined to be relevant to the delivery of an OAE removals project are accounted for in their most complete form.

Examples of Planetary project components may include:

**Scope 1**:

* Emissions from onsite electricity generation to run dosing and monitoring systems. Any Planetary owned energy generating devices.

**Scope 2**:

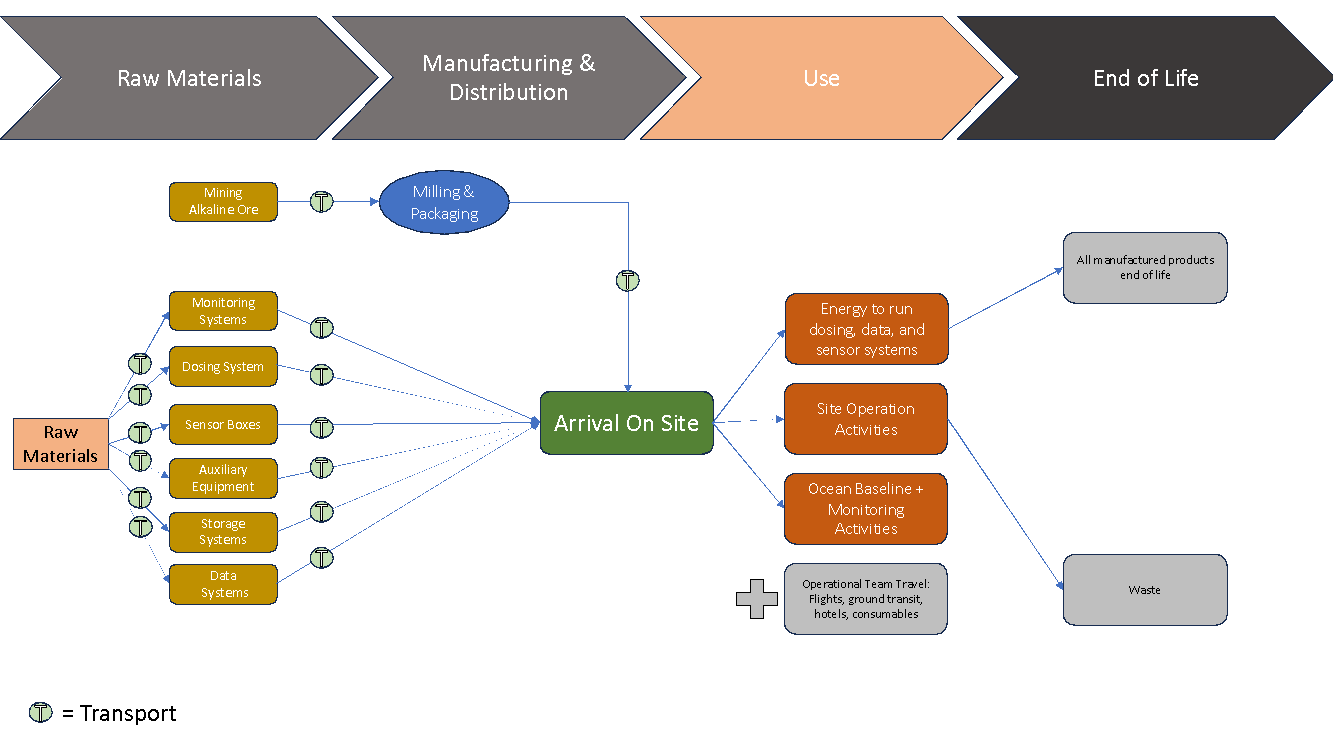
* Emissions from energy purchased or supplied to run project activities, whether generated externally or by the on-site host.

**Scope 3**:

* Alkaline feedstock embedded emissions.
* Embedded emissions in equipment manufacture and integration (i.e., pumps, hoses, tanks, electrical equipment) amortized over the equipment lifespan.
* Business travel required specifically for the project activity.
* Waste generated in our project operations.
* Any additional capital goods (amortized over the product lifespan).
* Any emissions generating services or goods used while on site.

The use of the United States Environmental Protection Agency scoping language is only to demonstrate the areas of minor or major contribution to the overall project footprint. The project GHG inventory will not be reported in this manner.  It is expected that Scope 3 components will be the most significant emissions areas due to external vendors and project partner activities, as well as hard to abate areas of project delivery.

Each component of the project scenario is broken out into its distinct phase through the lifecycle (see Figure 6). These phases are labeled as Raw Materials Extraction, Manufacturing and Distribution, Use, and End of Life. Significant to note between these phases is the transportation of those materials as they move towards their next phase.

**Figure 6;** Project scenario. 

## Time Boundary

Each project’s footprint and their individual campaigns will have a specific time boundary, which unless otherwise stated will also apply to the individual process. These boundaries will likely be expressed in months with a start and end day but will go up to one year.

However, from the day of alkalinity addition, the capture process is expected to vary depending on site conditions and modelled timelines.

## Functional Unit

In order to appropriately compare and contrast the baseline scenario with the project scenario, this protocol will utilize a functional unit or equivalent. The functional unit's purpose is to demonstrate equivalence in the type and level of activity for both scenarios.

It is expected that all projects will utilize the single metric tonne of alkalinity as a functional unit. While each project may use varying sources of alkalinity which each undergo different beneficiation and purification steps, it is Planetary’s expectation that CO2e/metric tonne alkalinity will be the most accurate reporting functional unit.

In the case of multiple operating campaigns occur at a single location, each campaign will be distinguished as a separate OAE removal activity.

## Alkalinity as a secondary product

In the case that alkalinity sourced for a project originates from a waste or secondary product of another process, Planetary will apply a cut-off approach. The use of these secondary products will be “burden-free” until any additional operation specifically applied to alkaline material must be accounted for (e.g. milling, grinding, transport, handling).

The burden free sourcing of secondary products will be limited to where a source has a limited quantity and no option to increase production of that alkaline material exists. In the scenario where secondary alkaline materials are being regularly produced, an annual average secondary production number will be established using supplier provided historical data. This annual average secondary production figure will establish the burden free cut-off point.

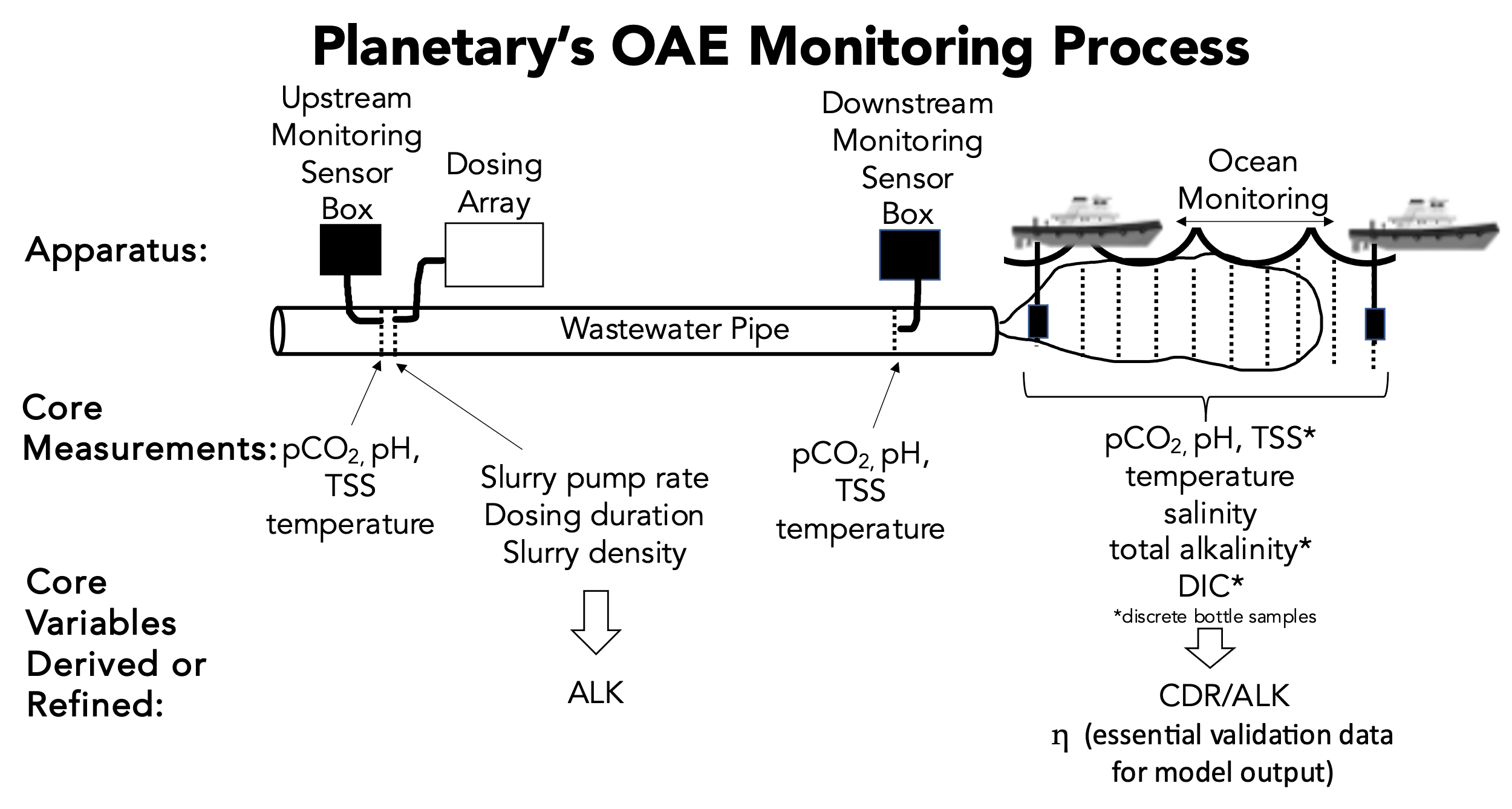
## Reporting as ELCA

While the project emissions report will include the use of the functional unit term, the final emissions figure for a campaign or given project timeline will be reported as the ELCA figure using units of total mass in metric tonnes CO2e (as shown in Equation (3)).

# Measurement and monitoring

In order to verify Planetary’s CDR, a core set of chemical and physical parameters (T, S, pH, DIC, TA, TSS) will be measured before, during, and after alkalization, and the resulting data set will be used to calculate all the variables in the fundamental CDR equations described above.

Figure 7 lists these raw measurements in a schematic that illustrates the proposed monitoring setup for wastewater discharges.



**Figure 7;** Schematic layout of Planetary’s monitoring program, the measurements made at each location, and the resulting parameters required for calculation of CDRMAX.

A site-specific monitoring plan will be developed and maintained for each project site, in accordance with the requirements set out in ISO 14064-2 (parag. 6.10).

## Measurement and monitoring of alkalinity dosing

The quantity of MH added (Equation (1)) is determined by continuous measurements of dosing rate and slurry properties at the point of dosing (Table 1).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Component** | **Value** | **σ** | **Units** | **Commentary** |
| Slurry pump rate |  |  | L/m | Calibration records |
| Dosing duration |  |  | hr |  |
| Slurry density |  |  | kg/m3 | Calibration records |
| Raw produce MH content |  |  | wt% | Periodic assay |
| Raw product density |  |  | kg/m3 | Periodic assay |
| Water density |  |  | kg/m3 |  |
| Slurry loading (wt% product) |  |  | % | Calculated from densities |
| **MH added** |  |  | **tMH** | **tMH during dosing period** |

**Table 1;** Measurements required to determine MH added and its uncertainty

Total life-cycle emissions (ELCA; Equation (3)) is determined by assessment of each component of the alkalinity supply chain;

|  |  |  |
| --- | --- | --- |
| **Component** | **Data source** | **Frequency** |
| Mining and comminution | Provided by supplier | Upon new source and every year |
| Transportation | Bill of lading, transport modes and distances, using standard emissions factors | Per shipment |
| Dosing and monitoring | Energy consumption and eqpt. embedded emissions | Upon installation or modification of dosing setup |
| **ELCA** |  |  |

**Table 2;** Components of ELCA; data source and frequency

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Component** | **Value** | **σ** | **Units** | **Commentary** |
| Product mining |  |  | gCO2/kg |  |
| Product comminution |  |  | gCO2/kg |  |
| Road distance |  |  | km |  |
| Road emissions rate |  |  | gCO2/t.km |  |
| Marine distance |  |  | km |  |
| Marine emissions rate |  |  | gCO2/t.km |  |
| Rail distance |  |  | km |  |
| Rail emissions rate |  |  | gCO2/t.km |  |
| Barge distance |  |  | km |  |
| Barge emissions rate |  |  | gCO2/t.km |  |
| Project emissions |  |  | gCO2/kg | Dosing and monitoring, other project specific emissions (e.g., travel) plus corporate allocation |
| **ELCA** |  |  | **gCO2/kg** |  |

**Table 3;** Measurements required to determine ELCA and its uncertainty

An estimate of the absolute uncertainty (σ) of each component—both for MH added and for ELCA—is required as input to the uncertainty analysis that will determine CDRHBACK.

## Measurement and monitoring of ocean geochemistry

The initial estimate of CDR/ALK (Equation (1)) is determined from ocean properties (T, S, pH, DIC) for the region over which air-sea equilibration will take place. Given the long timescale for equilibration, annual average values are appropriate, and representative values can be obtained from reanalysis products available from global and regional oceanographic databases[[29]](#footnote-29). Uncertainties in these inputs can be assessed from inter-year comparison.

CDR/ALK is calculated from these inputs using CO2SYS (or similar software) but, since there is no simple algebraic relationship it is not possible to use the addition of variance approach shown in Box 3 to estimate a σCDR/ALK. Given the small number of factors, this can most easily be done using a simple factorial design experiment (See Box 6).

***Box 6: Assessing the uncertainty in CDR/ALK using a factorial design experiment***

A reduced factorial design approach to determining the uncertainty in CDR/ALK involves simply running CO2SYS for the 7 cases shown below and calculating the standard deviation of the set of 7 values.

A chart of a number of letters

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For example, taking T = (12, 14, 16) °C, S = (31, 33, 35) ppt, pH = (8.0, 8.1, 8.2) (seawater scale), and equilibrated at pCO2 = 420 µatm gives;

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with a mean value of 0.851 and standard deviation of 0.124 (~ 1.5%).

Note that the L, M, and H should be equiprobable cases that reflect the possible range of values. There is no need for great precision here since we are just assessing the uncertainty in an initial estimate of CDR/ALK. Equally, a full factorial design covering the 27 (33) possible combinations could be run but would not significantly change the resulting estimate of the uncertainty in CDR/ALK.

The marine geochemical signal resulting from alkalinity addition (i.e., changes in pH, TA, DIC, pCO2) will not be measurable beyond a few meters from the discharge location until a significant scale is reached (probably in the 10s of kilotonnes of ALK per year), and quantitative analysis of the signal will be further confounded by the high natural variability. An effective ocean geochemical monitoring approach will be progressively developed as both sensor technologies advance and knowledge is gained through early field trials and modeling studies.

With this in mind, a site specific and nested set of ocean models are an essential part of monitoring, and ultimately calculating, CDR. Here, output of ocean models will determine the CDR efficiency, η (see Equation (A1.4)), which will be matched to a range of ocean data including project specific measurements and regional reanalysis products. Planetary’s cloud-based Ocean Carbon Calculator system will be used to consolidate the appropriate models and derive the CDR crediting schedule. Third-party verification of this system will be required to ensure accuracy.

## Monitoring of biological/ecological impact

Ecological safety cannot be guaranteed for any human activity that intersects the natural world, including alkalinity addition, and rigorous monitoring, building on the results of peer-reviewed studies, will be required to identify and mitigate any potential ecological concerns surrounding these activities.

As stated in Planetary’s published code of conduct[[30]](#footnote-30), a strong understanding of any environmental impacts, both positive and negative, is a primary measure of success. In turn, the Planetary team is dedicated to ensuring, to the greatest extent possible given current knowledge, that ecological risks are minimized.

### Current scientific understanding regarding biological/ecological impacts of OAE

Although academic literature regarding impacts of specific OAE activities on marine biota remains relatively sparse[[31]](#footnote-31), decades of research in highly relevant areas greatly help establish critical guardrails for OAE projects. This is especially true for Planetary’s OAE process, which utilizes regulated ocean outfalls with well-defined discharge limits for environmental protection in various jurisdictions. These limits cover key physical and chemical parameters, such as pH, total suspended solids (TSS) or turbidity, and heavy metal concentrations. Also, ecotoxicological impacts of alkaline materials like MH, bicarbonate ions, and trace metals across particular species are known. These limits are listed in Appendix 2, and provide absolute bounds that will not be exceeded.

Planetary’s choice of MH as the alkalinity source has significant beneficial implications for biological safety. MH is not classified as dangerous under the Workplace Hazardous Materials Information System (WHMIS) nor is it classified as persistent, bio-accumulative, or toxic under the Environmental Protection Agencies Toxic Release Inventory List or Toxic Substances Control Act[[32]](#footnote-32). Perhaps most importantly, MH is of low toxicity to aquatic organisms, with published limits greatly exceeding any concentrations Planetary is aiming to disperse into the ocean (see Appendix 2, Table A2.1). The European Chemicals Agency characterizes MH as follows;[[33]](#footnote-33)

*Magnesium hydroxide is of low acute toxicity to aquatic organisms and does not meet the criteria to be classified as dangerous under the CLP Regulation (EC) No 1272/2008 nor does it meet the criteria to be classified as persistent, bioaccumulative or toxic under the REACH Regulation.*

*Long-term toxicity of fish and aquatic invertebrates is unlikely to occur based on the physico-chemical properties of magnesium hydroxide, the breakdown pathway of the substance, the low acute toxicity and the fact that magnesium ions are ubiquitous in the natural environment. Therefore, according to REACH Annex IX, 9.1., column 2 there is no need to investigate further on the effects on aquatic organisms.*

*Magnesium hydroxide has a low potential to adsorb to sediment. Furthermore, magnesium hydroxide is expected to break down in the environment to water and magnesium over time. Magnesium is ubiquitous in the environment and is an essential plant and animal nutrient.*

Appendix 2 summarises the current state of scientific understanding of the biological and ecological impacts of OAE, including the results of studies into the impact of alkalinity perturbations. To date, these studies have provided further confirmation that, at alkalinity addition levels representative of Planetary’s OAE approach, the physiological impacts on a range of organisms are limited or undetectable.

An important characteristic of MH that greatly limits its potential environmental impact is its slow dissolution kinetics (i.e., its low solubility). Slow MH dissolution means that general dilution of the alkalized effluent in the marine environment will greatly outpace the chemical changes induced by the MH addition. The key example for this is pH, an important environmental quality standard (EQS) applicable to all discharges (see Appendix 2, Table A2.3). The relatively slow dissolution kinetics of MH will prevent any rapid pH rise at the dosing location, after which rapid dilution with ambient seawater will keep pH well within safe limits. This has been confirmed by controlled pool-scale experiments (at the Dalhousie Aquatron), where 4 probes located at differing proximities (1.5 m-13 m) from a pipe dosing saturated MH slurry measured maximum pH increases of 0.13-0.32 units.

### Monitoring ecological safety

In addition to the inherent mitigation factors noted above, close monitoring and control of alkalinity source materials and dosing rates alongside monitoring of important ecological parameters, such as pH and total suspended solids (TSS), will further ensure permit limits are strictly adhered to and environmental impact is minimized. Planetary is developing technology whereby a feedback loop within a central computing system allows for environmental data collected downstream (i.e., pH and/or TSS within the effluent, or potentially from a ship) to automatically tune the dosing rate. For example, if in-pipe pH measured downstream exceeds a given threshold near the permitting limit, dosing would automatically decrease or cease until the pH drops accordingly. Ocean monitoring will also provide a feedback loop for alkalinity addition, in that continued addition will depend upon monitoring data validating the working hypothesis that no or extremely limited impacts are detected in the receptors monitored.

This section discusses the core aspects of ecological monitoring scope that will be implemented at Planetary’s OAE deployments.

**Chemical characterization of alkalinity prior to release**

A crucial guardrail related to the possible presence of trace metal impurities in an alkalinity source is comprehensive elemental analysis prior to any alkalinity release, using certified methodologies and accredited laboratories. Once the levels of impurities are quantified, a screening workflow will be applied to determine maximum possible impurities levels in i) the wastewater discharge and ii) the receiving waters for a given project, taking into account dilution and background levels of impurities in both discharge and receiving waters. This information can be screened against the relevant regulatory limits for trace metals (see Appendix 2) and used to assess the viability of a given alkalinity source to deliver CDR while complying with these limits.

**Baseline monitoring**

Prior to the commencement of any project, baseline data will be gathered at the addition point and within the area likely to be most affected by alkalinity addition, with the aim of identifying any potential ecological responses that need to be monitored during OAE operations.

Baseline data collection will include measurements of background seawater carbonate chemistry, trace metals, physical water column parameters (T, S, pH, TSS), together with characterization of the marine community composition (including phytoplankton functional groups) and physical habitat structure present at the deployment location. Wherever possible, continuous data from constantly logging sensors will be preferred over discrete data.

The seafloor environment at the addition point will also be assessed. If present, seafloor sediments may be collected for chemical analysis, as well as characterization of the benthic infaunal and microbial communities. If possible, ecological assessments of benthic epifauna and epifloral may be conducted.

Existing baseline data will be collated from various sources alongside dedicated field survey effort, including through consultation with local partners, academic institutions, and public records. The temporal resolution of baseline data is important, as it should extend back far enough to establish seasonal variability.

**Development of a project specific ecological monitoring plan**

A monitoring plan will be developed for each operational site, based on the potential ecological responses to OAE identified from the baseline monitoring and following the general considerations summarized in the following table.[[34]](#footnote-34)

|  |  |
| --- | --- |
| **Monitoring aspect** | **Key considerations** |
| Monitoring frequency | Will depend on alkalinity addition rate, operational consideration, and data provided by previous monitoring (see adaptive management strategy below). Temporal resolution must be sufficient to detect any significant impacts to the identified receptors. |
| Siting of monitoring stations | Will depend upon the expected alkalinity perturbation and overall project scale; if the scale of the alkalinity perturbation is small or the signal is very dilute, environmental impacts will not likely be measurable far from where the perturbation takes place |
| Control locations | Control locations will provide reference points in order to separate natural variability in the marine environment from OAE impacts. Control sites should be closely analogous to the addition location in terms of bathymetry, benthic substrate, benthic habitats, current and tidal regime, and water column characteristics. Locations will be informed by site-specific conditions and modelling work, and should be sufficiently far from the addition point for monitored parameters to be representative of background conditions. |
| Trophic level focus | Any direct impacts arising from alkalinity addition will be most easily detected in lower trophic level organisms, due to shorter generation times and increased sensitivity to physical or chemical changes to the water and sediment. A focus on water and sediment quality, together with lower trophic level organisms, will therefore maximise the possibility of detecting any ecological impact from OAE. |
| Adaptive management | The project monitoring plan will incorporate adaptive management, so that gathered data will influence subsequent monitoring, directing these efforts towards detectable impacts on identified receptors. |
| Instrumental precision | At currently anticipated alkalinity addition rates, TA, pH, and pCO2 signals will only be detectable in the immediate vicinity of the addition site, particularly when considering the significant natural variability in these variables. |

**Operational monitoring**

Once alkalinity addition commences, regular monitoring will be conducted in line with the project monitoring plan. Comparison of operational monitoring data against both baseline records and control site data will allow for discernment of temporal and spatial trends.

Some ecological impacts may only become apparent over longer timescales, and Planetary is committed to carrying out follow-up monitoring throughout and beyond the operational phase of a given OAE deployment. The frequency and nature of this follow-up monitoring will be informed by any changes observed during the operational phase, and will be agreed through consultation with regulators, local partners, and stakeholders prior to the termination of the project.

### Monitoring restorative impacts

It is important to keep in mind the potential ecological benefits of alkalinity addition, namely its restorative chemical impact. OAE has been shown to enhance calcification rates in coral reef ecosystems[[35]](#footnote-35), although more research is needed to build on this conclusion. Such research is underway in partnership with Planetary, with the aim of assessing whether OAE leads to quantifiable increases in coral resilience to bleaching.

Monitoring this impact will be done predominantly using pH and carbonate saturation state. Specifically, mapping the magnitude and spatial extent of elevated pH (similar to mapping of pCO2 described above) will quantify the extent to which alkalinity addition has effectively countered ocean acidification in the local environment. Also, using bottle samples of DIC and TA, we anticipate measuring localized increases in the calcite and aragonite saturation states (Ωcalcite, Ωaragonite) a parameter which describes the extent to which seawater is corrosive to (Ω < 1) or preservative of (Ω > 1) carbonate shell-forming organisms. Subsequently, these data will also be used to validate models that predict the extent to which pH and carbonate saturation states are increased both locally and downstream of the addition site.

# Reporting

## Reporting requirements

Project reporting supports the verification of the amounts of carbon dioxide removed, including the accuracy of critical measurements that underpin the calculation. A project reporting procedure will be developed, in line with ISO14064-2 (parag. 6.13), and incorporating the following additional requirements;

1. As noted above, the LCA emissions of the alkalinity used in the process will be properly audited - either directly by the 3rd party or through reliance on a trusted external verifier.
2. The transportation emissions will be assessed from transit paperwork.
3. Records of periodic assays for the MH product used will include, but not be limited to, particle size distribution (PSD), heavy metal content, and %MH.
4. The dosing records will be reviewed and matched to delivery load amounts. Parameters closely monitored will include, but are not limited to:
   1. pH
   2. TSS
   3. alkalinity dosing rate and duration
   4. slurry concentration/density
5. Metering must be shown to be accurate and reliable, via appropriately certified calibration records.
6. The pCO2 sensing results will be reviewed.
7. Numerical models will be validated with relevant ocean sensing data.
8. Modeling reports will document input parameters, summary of model outputs, overall performance (relative to validation data), and basis for any time cut-off applied to η.
9. The calculation of net and creditable CO2 removed (i.e. output of Planetary’s Ocean Carbon Calculator) will be assessed by the verifier on a regular time interval.
10. Uncertainty analysis, including probability distribution parameters (mean, standard deviation, skewness, etc.) of calculation inputs, will be reported to the verifier for independent assessment of CDRHBACK and CDRCRED.

## Data management

In line with our commitment to share the results of field tests and deployments, Planetary is developing a cloud-based data management system that will provide open-access to related project data.

Data generated at our operating sites will include;

1) Alkalinity dosing system and associated sensor platforms

2) Discrete measurements for sensor calibration and drift correction

3) Data supporting the calculation of LCA emissions, following third-party review.

4) Numerical model outputs, calibration data (e.g., ocean and climatological measurements, and ocean re-analysis product outputs), and related OAE efficiency calculations.

5) Biological/ecological measurements and monitoring results (including notebooks and videos).

Data from the alkalinity dosing system and its associated sensors will be available in real time, while other types of quality-controlled data will be uploaded to the cloud-based data center, with an upload target within one week of collection to allow timely analysis, visualization, and interpretation. The data management system will provide version control for numerical model outputs, which underpin the determination of CDRGROSS, to be updated every one to two years based on hindcast matching of the project model to the actual regional climatology.

Automatic tools will be developed to assist in data screening and quality-control, and completed data records will be stored and maintained by Planetary’s Data Management team, with a retention period of at least 10 years.

Data management procedures will be developed and maintained to ensure the quality of published data, and will include regular checks for accuracy and the elimination of technical errors, the periodic conduct of internal audits and technical reviews, and the appropriate training of project team members with data management responsibilities.

We also plan to develop and maintain a dashboard to allow easy access and visualization of project data and statistical information, and to publish an annual report that concisely summarizes and shares project data via a number of data metrics.

# Verification

*Isometric verification process is under development and will be summarised here*

… verification is performed by an independent third party against this MRV plan.

# Future directions

The reduction of uncertainty will be a major aim in the further development of this protocol, which will focus on a number of areas;

Supply chain emissions; the complex nature of the emissions portfolio for a given project (illustrated in Figure 6) can lead to large propagated uncertainties on the final ELCA term. As projects mature, further investigation into these emissions sources coupled with more established supply chains and additional third party auditing should lead to considerable uncertainty reduction. Experiences gained and tools built in early projects should reduce the initial uncertainties for future projects.

Surface residence time of alkalized water; particularly in deployment locations where the residence timescale of surface waters is comparable to the timescale of air-sea CO2 equilibration, accurate representation of the seawater flow and circulation will be an important requirement for model validation[[36]](#footnote-36). Datasets of direct ocean measurements are often sparsely populated but, at increasing deployment scale, the dedicated acquisition of regional ocean data for model calibration may become economically viable. Ultimately this could include the direct measurement of the seawater carbonate system perturbation on a regional scale (after extensive baselining) and perhaps the direct measurement of enhanced air-sea CO2 flux. Observing system simulation experiments (OSSEs) will be a key tool to optimize the information vs. cost of such monitoring systems32.

Biogeochemical impacts; As discussed in Section 2.4, biogeochemical responses such as secondary precipitation and enhanced biocalcification are expected to have minimal impact on CDR effectiveness. Further research will be needed to determine whether the current understanding of these impacts continues to hold at increasing deployment scale, and to design effective monitoring and/or mitigation approaches if these are required. Similarly, the volume of peer-reviewed literature regarding the ecosystems effects of OAE is expected to increase dramatically in the coming year, which will help to further refine biological monitoring efforts across our various sites.

Mineral particle dissolution rate; Depending on local oceanographic conditions, the relatively slow dissolution rate of MH particles in the 10µm size range could lead to the sinking of undissolved particles below the deepest seasonal mixed layer depth, reducing CDR efficiency. A Lagrangian particle tracking approach is currently under development to quantify and locate (in space and time) the release of alkalinity from advecting, sinking, and dissolving particles of a generic size distribution. This will provide a basis for assessing the magnitude of any such loss.

# Acknowledgements

**Planetary team**

**Technical contributors**

|  |  |
| --- | --- |
| Will Burt PhD | Tim Cross MSc |
| Brenan Duhamel MSc, MRes | Robert Izett PhD |
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**Non-technical contributors**

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**External reviewers**

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**Element Energy and E4Tech (ERM group companies)**

As part of an independent review of existing MRV standards for the UK Government Department for Energy Security and Net Zero (DESNZ).

**Isometric**

|  |  |
| --- | --- |
| Sophie Gill PhD | Jing He PhD |
| Kevin Sutherland PhD |  |

**Ocean Visions**

TBD

**Project Vesta**

Grace Andrews PhD

# Appendix 1; Discussion of factors affecting CDR determination

## A1.1 CDRMAX

CDRMAXrefers to the theoretical maximum CDR achieved without considering potential losses or inefficiencies in the fundamental OAE process. In the case of Mg(OH)2 addition, CO2 is removed from solution via the reaction;

Mg2+ + 2OH¯ + *A*(CO2aq) → Mg2+ + *B*(HCO3¯) + *C*(CO32-) + *D*(OH¯) (A1.1)

where *A* = *B* + *C* and *B* + (2 x *C*) + *D* = 2. At a typical equilibrium seawater pH of 8.1 at 20 °C, 35 ppt salinity and at near sea surface pressure (typically taken as 10 dbar), *A* = 1.65 mols of CO2 per mol of MH, which equates to a CDRMAX versus added alkalinity mol ratio (CDRMAX/ALK) of 1.65/2 = 0.825 considering that 1 mol MH = 2 mols alkalinity. *B*, *C* and *D* are 1.48, 0.17 and 0.18 moles per mol of Mg(OH)2aq, respectively under these ocean conditions, based on seawater chemistry modeling using CO2SYS[[37]](#footnote-37).

These preceding molar ratios vary as a function of equilibrium seawater pH, temperature (T) and salinity (S). In particular, the molar quantity *A* decreases (increases) with increasing (decreasing) equilibrium seawater pH, T and S (Figure A1.1). The reason for this is that the CO32- fraction of the total dissolved inorganic carbon (DIC) in a solution increases as these parameters increase. Because this is a divalent ion, it takes twice the alkalinity to charge balance and store than for the more abundant, monovalent HCO3¯ ion. This accordingly reduces the CO2 consumption and storage efficiency per mole of alkalinity addition. In the extreme, as pH declines the CDRMAX/MH molar ratio asymptotes to 2, as the reaction becomes predominantly;

Mg(OH)2 + 2CO2 → Mg2+ + 2HCO3¯ (A1.2)

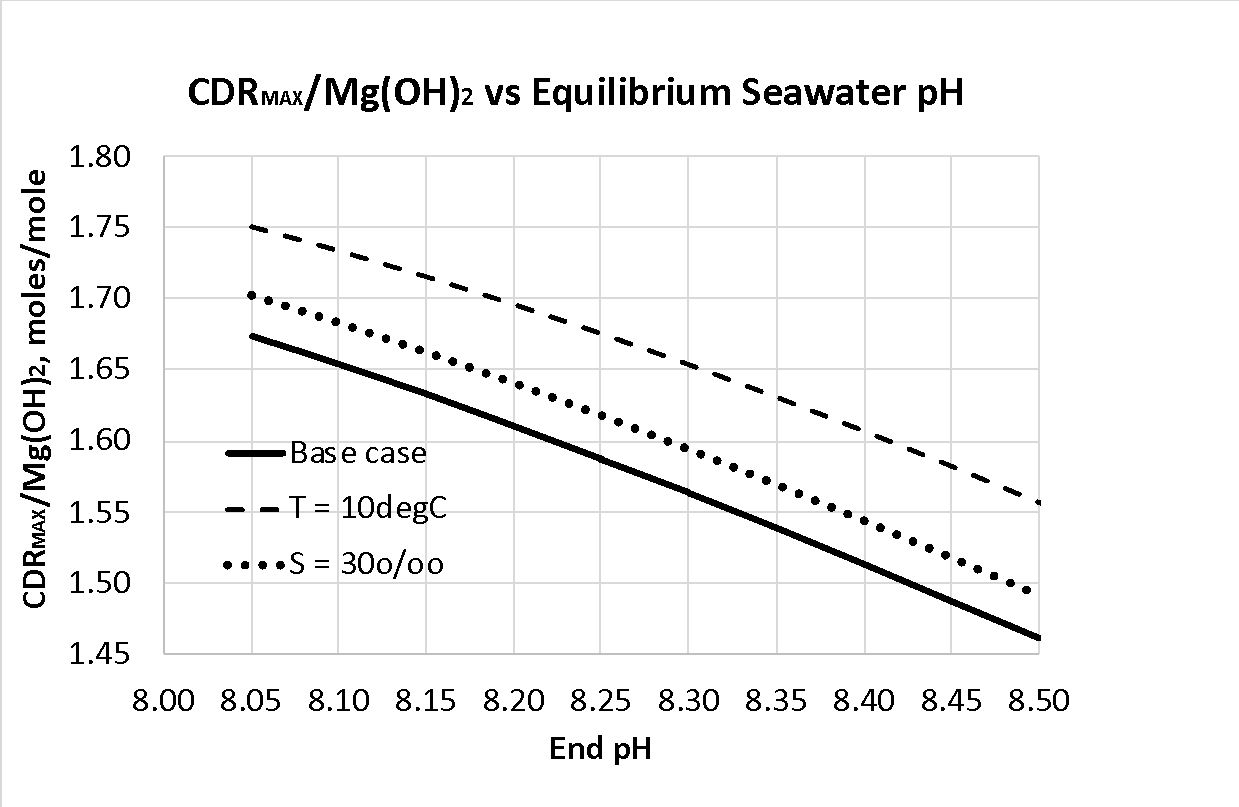
Conversely, *A* approaches 1 as pH rises and the dominant reaction becomes;

Mg(OH)2 + CO2 → Mg2+ + CO32-  (A1.3)

The CDRMAX/MH molar ratio thus maximally ranges from 1 to 2 (corresponding to a CDRMAX/ALK molar ratio range from 0.5 to 1).

In terms of mass, 1.65 (mols CO2/mol MH) x 44 (wt./mol CO2)/58.3 (wt./mol MH) = 1.25 t CO2/t MH at a pH of 8.1. Thus, by knowing the total tonnes of MH added to the surface ocean mixed layer we can calculate the potential gross CDR achieved at a final ocean equilibrium pH (Figure A1.1). These conditions are approximated by the mean, background pH, T, and S of the surface seawater into which the alkalinity is to be added and (effectively infinitely) diluted.

Tyka and colleagues[[38]](#footnote-38) suggested that the typical CDRMAX/ALK value is ~0.8, which equates to a CDRMAX/MH of 1.6. A CDRMAX/ALK ratio of 0.83 has been derived and used by Renforth and Henderson[[39]](#footnote-39) to investigate the scale of carbon sequestration through increasing ocean alkalinity. In addition, a recent model simulation of OAE in the Bering Sea reveals that the CDRMAX/ALK ratio is on the high end (≥0.85) because of high DIC and persistently low pH and T in the study region[[40]](#footnote-40).



**Figure A1.1;** Change in the CDRMAX/MH added molar ratio (= 2 x Delta [DIC]/Delta [TA]) as a function of ocean pH under air pCO2 equilibration, where pCO2 is held constant at 415 µatm and pH is increased by 0.05 units from 8.00 to 8.50. The resulting change in DIC relative to change in alkalinity at each pH step is then determined. Base conditions: S = 35 ppt, T = 20 °C, P = 10 dbar. The effects of decreasing S and T from the base case are shown; modelled using CO2SYS.

## A1.2 CDR efficiency

As defined by Equation (2), ηis the fraction of the theoretical CDRGROSS that is achieved for a specific location, and is derived from numerical ocean modeling (methods for which are discussed below). Thus, CDR efficiency (η) is given by;

η = CDRMODEL / CDRMAX  (A1.4)

where CDRMODEL is the gross CDR calculated from a project specific ocean model, which accounts for the potential loss of added alkalinity due to;

1. sinking of undissolved alkaline particles out of the surface mixed layer such that dissolved alkalinity generation, CO2 depletion, air contact, and CDR does not occur within a climate relevant time period, and
2. advection of alkalized, CO2-depleted seawater out of contact with the atmosphere such that CDR does not occur within a climate relevant time period.

Both of these loss terms are to some degree temporary, since global ocean circulation and upwelling will eventually bring the “lost” alkalinity back into contact with the ocean surface. However, the ocean circulation time of at least several centuries rules this out as not “climate relevant”. Other potential loss terms may exist, including MH particle ingestion by organisms or the neutralization of non-carbonic acids by the added MH, but these loss terms will be vastly smaller in magnitude, and thus are not considered at this time.

It is important to note that, while a preliminary CDRMAX may be calculated using a CDR/ALK determined from estimated average conditions (pH, T, S) over the ocean area in which CDR takes place, CDRMODEL will be determined by the ocean conditions calculated within the model, based on the prescribed initial conditions, conditioned by the imposed climatology, and matched to the best available actual ocean data. CDRGROSS ( = CDRMAX x η) will therefore not depend on the initial estimate of average ocean conditions. If a value for η is calculated using a preliminary CDRMAX (based on “typical” seawater conditions), this will be an approximation—subject to an uncertainty on the order of a few percent. A more accurate value for η as a true “efficiency”—for example to compare projects—would require the CDR/ALK ratio to be calculated from the model.

Published and in-house laboratory experiments and models, demonstrate that dissolution of fine MH particles in seawater occurs on timescales of hours to weeks[[41]](#footnote-41), while reported timescales for ocean-atmosphere CO2 equilibration range from weeks to months[[42]](#footnote-42),[[43]](#footnote-43),[[44]](#footnote-44),[[45]](#footnote-45). The 1-year time horizon for η proposed in Version 2 of this protocol aligned well with CO2 equilibration timescales (e-folding times), modeled by Jones and colleagues38, who reported a global mean value of 4.1 months with a standard deviation of 3.4 months, and only a small fraction of areas in offshore waters where the value exceeded 12 months. That study revealed deeper mixed layer depth (MLD), offset by higher winter wind speeds, as the dominant factor driving increases in equilibration timescales, highlighting the importance of understanding these specific dynamics near a proposed OAE site.

Planetary’s OAE approach centers on alkalinity addition to relatively shallow coastal/near shore areas, inherently lowering the risk of alkalized waters reaching deep offshore prior to equilibration. Nevertheless, Planetary’s in-house modeling work has confirmed the strong influence of MLD on η also in coastal seas, and particularly the seasonal ML dynamics – rapidly shoaling in late spring and gradually deepening in autumn. Depending on site-specific conditions, the spring MLD shoaling can result in “seasonal trapping”, where some fraction of the released alkalinity is effectively isolated from the ocean surface until the MLD deepens again in the autumn, and alkalized, pCO2 depleted water is again brought back into contact with the ocean surface. As a result of this effect, and depending on site specific condition—notably the water depth—η values above 90-95% are likely to require two or more shoaling-deepening cycles. This is illustrated in Figure A1.2 which shows the evolution of η derived from a 1D diffusivity model, based on conditions representative for the SW UK shelf waters (100 m water depth), as well as the seasonal MLD dynamics and average windspeeds. In this example alkalinity is added over a 14-day dosing period in June.

A graph showing a line of different sizes

Description automatically generated

**Figure A1.2;** Illustrative example of seasonal MLD, average windspeeds, and resulting η evolution in SW UK shelf waters.

These results demonstrate that accurate, project level CDR assessment requires a different perspective from the simple e-folding equilibration timescales derived from global ocean models. As such, no specific time horizon is proposed for determining η and thence CDRGROSS. This will be assessed on a project-by-project basis, depending on location specific ocean conditions, and will be documented in modeling reports.

Bach and colleagues recently proposed a 10-year time horizon as a possible cut-off for CDRGROSS[[46]](#footnote-46), although the authors noted that any such cut-off is ultimately arbitrary. Nevertheless, the uncertainty in model results will inevitably increase as the elapsed time from alkalinity release to air-sea equilibration (and eventual subduction) increases, and such a cut-off is consistent with the need for high confidence in credited volumes.

**Modeling approaches**

Planetary has used a number of modeling approaches in assessing CDR for early field trials and in developing this protocol, ranging from full 3D models driven by actual climatologies (insolation, windspeed, freshwater inputs, etc.) to a simple 1D water column model with externally imposed vertical diffusivities and MLD dynamics (i.e., not driven by physics encoded in the model) but using actual windspeed data to drive a realistic air-sea CO2 flux.

For 2D and 3D modeling, both commercial (e.g., Delft 3D suite) and academic community (e.g., ROMS, FVCOM) software products have been used, with, in the former case, new modules coded to include additional features such as particle dissolution, ocean carbonate chemistry, and air-sea flux. Adequate representation of the dissolution and sinking of mineral particles is a specific challenge in modeling Planetary’s OAE approach, and a novel approach to this problem—based on Lagrangian particle tracking—is under development.

A simple 1D water column model has also proved valuable in testing sensitivities, for example to windspeed and windspeed averaging, MLD, vertical diffusivity, etc. This simple model has also revealed the important interaction between the mixed layer shoaling/deepening cycle and the time profile of CO2 equilibration, described above. It is envisaged that calibration of 1D results against 3D model outputs will allow a wider range of sensitivities to be investigated at minimal computing cost.

At most project sites, 3D regional models will be required to capture the full range of processes affecting CDR efficiency. These models will be calibrated using direct ocean measurements (where available) or using the output from ocean reanalysis products, which are in turn matched to the best available regional datasets (including, for example, satellite remote sensing). Standard metrics for assessing the performance of coastal hydrodynamic models are well established, based on long industry practice,[[47]](#footnote-47) but modeling for OAE CDR, particularly at the project level, is still in its infancy. Assessment criteria for OAE project models—identifying when a model is deemed “good enough”—will be progressively established as the body of experience with such models grows.

Planetary’s Ocean Carbon Calculator is a tool that consolidates these approaches and other emerging approaches to modeling OAE in order to provide a consistent and verifiable calculation of air-sea flux change and the associated uncertainty of these approaches. With this approach, verifiers can fully audit the model interpretation.

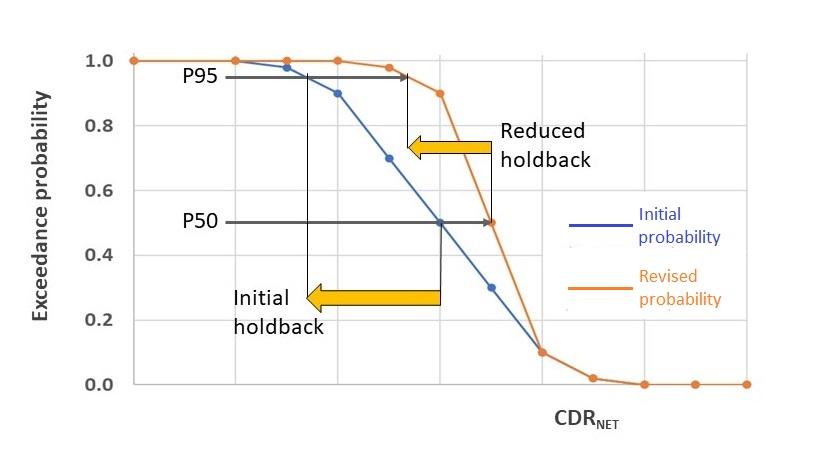
Going forward, further numerical modeling efforts that build upon and apply prior research to OAE-focused questions—both led by Planetary but perhaps more so by the greater research community—will undoubtedly help refine many aspects of these modeling approaches.

## A1.3 CDRHBACK

Version 2 of this protocol defined CDRHBACK as a fractional reduction in η, designed to allow solely for uncertainties in that factor, but also recognised that an uncertainty propagation exercise, taking into account the uncertainties for all relevant terms in Equations (1) to (3), would provide an alternative approach to quantifying this holdback. The uncertainty analysis discussed above in Section 2.3 now provides the basis for that broader definition of CDRHBACK as a discount to reflect the impact of end-to-end uncertainties on CDRNET.

Similarly, increasing confidence in the ocean model as it is validated against a growing body of direct ocean measurements, is now just one factor influencing the expected reduction in CDRHBACK over time. Improved accounting of ELCA is equally if not more important in the short to medium term, until the alkalinity supply chain becomes well controlled and audited.

Progressive reduction of all uncertainties will lead to a steepening of the CDRNET probability of exceedance curve, as illustrated in Figure A1.3, leading to a correspondingly reduced discount from the mid-case (shown as P50) to a high confidence CDRCRED.



**Figure A1.3:** Reducing CDRHBACK due to a reduction in combined uncertainties.

Note that in the example shown the mid-case value is also increased as uncertainties are reduced; this is done for visual clarity in the figure, and will not necessarily be the case.

Given its dependence on all end-to-end uncertainties, it is not possible to specify a simple underlying “schedule” for reducing CDRHBACK, as was outlined in Version 2 of this protocol. A reduction is as likely to arise as a result of improved control and auditing of the transport mode for alkalinity supply as it is from improved model validation. We envisage that project models will be updated (probably annually) with actual climatology and LCA data, reducing uncertainty in the prior year’s CDRNET, and allowing some of the holdback to be credited.

# Appendix 2: Biological and ecological monitoring considerations

## A2.1 Ecotoxicology

While the response of marine organisms to alkalinity perturbations remains a relatively nascent and continually evolving field (summarized in section A2.4), ecotoxicological studies and their resulting thresholds provide critical guardrails for consideration when developing OAE. Indeed, it appears that in some jurisdictions (e.g., Canada), clear compliance with ecotoxicological limits is often the primary concern.

**Ecotoxicology of MH**

Magnesium hydroxide (MH) is the selected alkalinity source for Planetary’s initial OAE deployments. It is considered to have low short-term toxicity to aquatic organisms, including fish, invertebrates, and algae, as well as to microorganisms. Published ecotoxicological guideline values from the European Chemicals Agency (ECHA, 2023) are summarized in Table A2.1, which indicate No Observed Effect Concentrations (NOEC) of at least 100 mg/L for algae and microbes, and EC50 thresholds of >100 mg/L for algal growth and biomass inhibition, and for microbial respiration inhibition. For fish, the LC50 dose is at least 307 mg/L for the fathead minnow (*P. promesas*) according to one study and likely higher, given that other studies assigned greater confidence by the ECHA recorded LC50 values of 1298 and 1366 mg/L for the same taxon. The ECHA summary on the acute toxicity of MH is as follows (ECHA, 2023):

*Magnesium hydroxide is of low acute toxicity to aquatic organisms and does not meet the criteria to be classified as dangerous under the CLP Regulation (EC) No 1272/2008 nor does it meet the criteria to be classified as persistent, bioaccumulative or toxic under the REACH Regulation.*

Alongside the summary of potential acute toxicity, the ECHA also provide an assessment of potential longer-term toxicity of MH in aquatic environments.

*Long-term toxicity of fish and aquatic invertebrates is unlikely to occur based on the physico-chemical properties of magnesium hydroxide, the breakdown pathway of the substance, the low acute toxicity and the fact that magnesium ions are ubiquitous in the natural environment. Therefore, according to REACH Annex IX, 9.1., column 2 there is no need to investigate further on the effects on aquatic organisms.*

The ecotoxicology dossier provided by ECHA also notes that:

*Magnesium hydroxide has a low potential to adsorb to sediment. Furthermore, magnesium hydroxide is expected to break down in the environment to water and magnesium over time. Magnesium is ubiquitous in the environment and is an essential plant and animal nutrient.*

In light of the benign nature of magnesium hydroxide and its limited and highly controlled addition rate during Planetary’s OAE process, the working hypothesis underpinning all alkalinity addition is that no detectable adverse impacts will be recorded in the marine environment. Nonetheless, the precautionary principle and Planetary’s own code of conduct demand that comprehensive and effective monitoring be undertaken to validate and confirm this.

**Table A2.1 Short-term ecotoxicological thresholds for magnesium hydroxide**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Organism Type | Species | Test & Duration | Effect  Conc. (mg/L) | Notes |
| Fish, freshwater | Brook trout (*Oncorhynchus mykiss*) | LC501, 96h | 776 | Effect conc. recalculated from test with 61% Mg(OH)2 solution to 100% |
| Fish, freshwater | Fathead minnow (*Pimephales promesas*) | LC50, 96h | 1,298 | Effect conc. recalculated from test with MgCl2 |
| Fish, freshwater | Fathead minnow (*Pimephales promesas*) | LC50, 96h | 1,366 | Effect conc. recalculated from test with MgSO4 |
| Fish, freshwater | Fathead minnow (*Pimephales promesas*) | LC50, 96h | 307 | Effect conc. recalculated from test with 60% Mg(OH)2 solution to 100% |
| Invertebrate, freshwater | Water flea (Daphnia magna) | LC50, 48h | 815 | Effect conc. recalculated from test with MgCl2 |
| Invertebrate, freshwater | Water flea (*Daphnia magna*) | LC50, 48h | 882 | Effect conc. recalculated from test with MgSO4 |
| Microalga, freshwater | *Raphidocelis subcapitata* | EC50growth2, 72h | >100 | EC50 for growth rate > 100 mg/L |
| Microalga, freshwater | *Raphidocelis subcapitata* | EC50yield3, 72h | >100 | EC50 for yield inhibition > 100 mg/L |
| Microalga, freshwater | *Raphidocelis subcapitata* | NOEC4, 72h | 100 | No observed effect concentration is 100 mg/L |
| Microbiology | Activated wastewater sludge | EC505respiration, 3h | >100 | EC50 for respiration rate >100 mg/L |
| Microbiology | Activated wastewater sludge | NOEC, 3h | 100 | No observed effect concentration is 100 mg/L |

|  |  |
| --- | --- |
| All ecotoxicology information sourced from [European Chemicals Agency dossier on magnesium hydroxide](https://echa.europa.eu/registration-dossier/-/registered-dossier/16073/6/1) | |
| 1 | Lethal Concentration 50: analyte concentration at which 50 % mortality of the test population occurred |
| 2 | Effect Concentration 50 Growth: analyte concentration at which 50% growth inhibition occurred relative to a control |
| 3 | Effect Concentration 50 Yield: analyte concentration at which 50% biomass yield inhibition occurred relative to a control |
| 4 | No Observed Effect Concentration: highest analyte concentration at which no significant effects were observed on a test population |
| 5 | Effect Concentration 50 Respiration: analyte concentration at which 50% of the test population experienced significant biomass yield inhibition relative to a control |

**Ecotoxicology of bicarbonate**

OAE results in the uptake of additional atmospheric CO2, and in turn higher concentrations of bicarbonate ions. Bicarbonate is one of the most abundant ions in seawater, suggesting that organisms may have a high tolerance for any increases in bicarbonate ion. Indeed, an ecotoxicology study into the effects of elevated DIC and bicarbonate ion concentrations revealed thresholds > 10mM across 8 different marine organisms spanning all trophic levels from bacterium to fish (Gim et al., 2018). These concentrations, summarized in Table A2.2 far exceed any anticipated OAE perturbations, even at the highest scales of deployment.

**Table A2.2 Ecotoxicology thresholds for bicarbonate ions on various marine organisms**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Taxon and Species | DIC  Conc. Range (mM) | Bicarbonate Conc. Range (mM) | Endpoint | Metric | Threshold (mM DIC) |
| Bacterium *Vibrio fischeri* | 3 – 190 | 2.8 – 180 | Luminescence inhibition | EC50 | No inhibition observed |
| Microalgae Various spp. | 3 – 180 | 2.8 – 170 | Growth rate inhibition | EC50 | 20 – 85 |
| Copepod *Tigriopus japonicus* | 3 – 170 | 2.8 – 160 | Mortality | LC50 | 11 |
| Rotifer *Brachions plicatilis* | 4 – 140 | 3.8 – 140 | Mortality | LC50 | 14 |
| Amphipod *Monocorophium acherusicum* | 3 – 170 | 2.9 – 160 | Mortality | LC50 | 14 |
| Echinoderm *Strongylocentrotus nudus* | 3 – 140 | 3.0 – 130 | Fertility inhibition | EC50 | 22 |
| Bivalve *Crassostrea gigas* | 5 – 180 | 4.9 – 170 | Mortality | LC50 | 41 |
| Fish *Cyprinodon variegatus* | 4 – 190 | 3.1 – 190 | Mortality | LC50 | 56 |
| Adapted from Gim et al. (2018). Potential ecotoxicological effects of elevated bicarbonate ion concentrations on various marine organisms. Environmental Pollution. 241. 194-199. 10.1016/j.envpol.2018.05.057. | | | | | |

## A2.2 International standards and thresholds

The following sections present a summary of international regulatory standards and thresholds for pH, total suspended solids and/or turbidity, and trace metals in aquatic environments, which are designed to minimize any adverse environmental impacts. Wherever possible, threshold values have been provided for marine environments; where freshwater values are provided this is clearly indicated. The guideline values listed are considered hard limits which, after appropriate consideration of dilution in discharge and receiving waters – (see below), Planetary’s alkalinity addition process must respect at all times. Given that a range of values are presented from various jurisdictions around the world, the relevant guideline value for the jurisdiction in question will be the most relevant standard for a given project. That said, screening comparison against a range of international thresholds provides helpful context and ensures that potentially outdated legislation in one jurisdiction is not used as a means to circumvent internationally accepted best practice.

**pH**

Guidelines values for pH in Canadian, US, Australian and British marine waters are defined below in Table A2.3. There is general agreement across most jurisdictions on a core acceptable range for pH, with some variation at the extremes. Of note is that both the Canadian and US regulations stipulate that pH should not vary by more than 0.2 units from the naturally occurring variation. -

**Table A2.3 International guideline value for pH in marine waters**

|  |  |  |  |
| --- | --- | --- | --- |
|  | Acceptable Range | Notes | |
| CCME1 | 7.0 – 8.7 | The pH of marine and estuarine waters should fall within the range of 7.0 - 8.7 units unless it can be demonstrated that such a pH is a result of natural processes. Within this range, pH should not vary by more than 0.2 pH units from the natural pH expected at that time. Where pH is naturally outside this range, human activities should not cause pH to change by more than 0.2 pH units from the natural pH expected at that time, and any change should tend towards the recommended range (CCME 1996). | |
| BC Min. Env. CC2 | 7.0 – 8.7 | Long term chronic - unrestricted change when pH is greater than 7 and less than 8.7 to protect mollusc embryo development. | |
| US EPA3 | 6.5 – 8.5 | For open ocean waters where the depth is substantially greater than the euphotic zone, the pH should not be changed more than 0.2 units from the naturally occurring variation or any case outside the range of 6.5 to 8.5. For shallow, highly productive coastal and estuarine areas where naturally occurring pH variations approach the lethal limits of some species, changes in pH should be avoided but, in any case, should not exceed the limits established for fresh water, i.e., 6.5-9.0. | |
| ANZECC4 | 8.0 – 8.4 | SE Australia | Default trigger values for pH for slightly disturbed ecosystems in given region |
| Tropical Australia (inshore) |
| SW Australia (inshore) |
| 8.0 – 8.5 | South Central Australia |
| UK EQS5 | 6.0 – 8.5 | Default limits for 95th percentile Maximum Allowable Concentration (MAC) operational environmental quality standard (EQS) for estuarine and coastal waters | |

|  |  |
| --- | --- |
| 1 | [Canadian Marine Water Quality Guidelines](https://ccme.ca/en/summary-table) developed by Canadian Council for Ministers of the Environment (CCME) |
| 2 | [Ambient Water Quality Guidelines (AWQG)](https://www2.gov.bc.ca/gov/content/environment/air-land-water/water/water-quality/water-quality-guidelines/approved-water-quality-guidelines) from the British Columbia Ministry of Environment and Climate Change |
| 3 | US EPA (1986) Quality Criteria for Water (“Gold Book”): Office of Water Regulations and Standards, EPA-440/5-86-001, USEPA, Washington DC. |
| 4 | Default trigger values from [Australian and New Zealand Guidelines for Fresh and Marine Water Quality, 2000.](https://www.waterquality.gov.au/anz-guidelines/resources/previous-guidelines/anzecc-armcanz-2000) |
| 5 | [Estuaries and coastal waters specific pollutants and operational environmental quality standards](https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/1000956/Estuaries_and_coastal_waters_specific_pollutants_and_operational_environmental_quality_standards.ods), UK Environment Agency |

**Total suspended solids and turbidity**

Guidelines values for TSS and turbidity in Canadian, US, Australian and British marine waters are defined below in Table A2.4. Of note is that in Canadian regulations, the acceptable TSS/turbidity variation is dependent upon characterization of background levels; in clear flow scenarios the acceptable variation is less than in turbid conditions. Three tiers of background turbidity are set out in British Columbian ambient water quality guidelines, whilst two tiers for TSS are defined by the CCME regulations. For clear flow scenarios, there are also separate guidelines for short term acute (up to 24 hours) and long term chronic (24 hours to 30 days) thresholds. -

**Table A2.4 International guideline values for turbidity/total suspended solids (TSS) in marine waters**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Parameter | Guideline Values | | |
| Background | Duration | Limit |
| CCME1 | TSS | Clear flow (< 25 mg/L) | Short term (up to 24 hrs) | Maximum increase of 25 mg/L over background |
| Long term (24 h - 30 days) | Maximum average increase of 5 mg/L from background |
| TSS | High flow (25 – 250 mg/L) | Any | Max. increase of 25 mg/L or 10% of background not exceeding 250 mg/L |
| BC Min. Env. CC2 | Turbidity | Clear flows or in clear waters (<8 NTU) | Short term acute (up to 24 hrs) | Change from background of 8 NTU6 |
| Long term chronic (up to 30 days) | Change from background of 2 NTU |
| 8 – 50 NTU during high flows or in turbid waters | Any | Max change of 5 NTU from background |
| Max change of 10% from background | Any | Change from background of 10% |
| US EPA3 | Turbidity /TSS | All | Any | Up to 10% reduction in seasonally established photic zone depth for aquatic life. |
| ANZECC4 | Turbidity | Tropical Australia estuarine and coastal waters | Any | 1 – 20 NTU |
| South-east Australia estuarine and coastal waters | 0.5 – 10 NTU |
| South-west Australia estuarine and coastal waters | 1 – 2 NTU |
| South-central Australia estuarine and coastal waters | 0.5 – 10 NTU |
| UK EQS5 | TSS | All | Any | 100 mg/L |

|  |  |
| --- | --- |
| 1 | [Canadian Marine Water Quality Guidelines](https://ccme.ca/en/summary-table) developed by Canadian Council for Ministers of the Environment (CCME) |
| 2 | [Ambient Water Quality Guidelines (AWQG)](https://www2.gov.bc.ca/gov/content/environment/air-land-water/water/water-quality/water-quality-guidelines/approved-water-quality-guidelines) from the British Columbia Ministry of Environment and Climate Change |
| 3 | US EPA (1986) Quality Criteria for Water (“Gold Book”): Office of Water Regulations and Standards, EPA-440/5-86-001, USEPA, Washington DC. |
| 4 | Default trigger values from [Australian and New Zealand Guidelines for Fresh and Marine Water Quality, 2000.](https://www.waterquality.gov.au/anz-guidelines/resources/previous-guidelines/anzecc-armcanz-2000) |
| 5 | [Default limit for waste water discharge to surface waters](https://www.gov.uk/government/publications/water-companies-water-treatment-works-discharge-limits-for-environmental-permits/water-companies-water-treatment-works-discharge-limits-for-environmental-permits).UK Environment Agency |
| 6 | Nephelometric turbidity units (see Glossary) |

**Trace metals**

Ecotoxicology guideline values for trace metals in Canadian, Dutch, US and Australian marine sediments are defined below in Table A2.5, with explanatory on the toxicology thresholds used provided below the table in the footnotes. Many standards provide two values: a lower threshold where no or minimal adverse effects are recorded and a second, higher, threshold, where deleterious effects from the analyte in question begin to become more pronounced. The Dutch intervention values merit particular mention; these are not guideline upper limit values but rather analyte levels at which there is a serious risk of environmental harm. They should therefore be avoided at all cost. In general, the lower threshold values should be adhered to in order to minimize the risk of environmental harm.

-

**Table A2.5 International ecotoxicology guideline values for trace metals in sediment**

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | Field et al. (2002) | | ANZECC | | Dutch | | Canadian | | Long et al. (1995) | | Buchman et al. (2008) | |
| Analyte | Units | T201 | T501 | DGV2 | GV-High2 | Target3 | Intervention3 | TEL4 | PEL4 | ERL5 | ERM5 | AET6 | Bioassay endpoint7 |
| Aluminium (Al) | % |  |  |  |  |  |  |  |  |  |  | 1.8 | N |
| Antimony (Sb) | mg/kg | 0.63 | 2.4 | 2 | 25 | 3 | 15 |  |  |  |  | 9.3 | E |
| Arsenic (As) | mg/kg | 7.4 | 20 | 20 | 70 | 0.9 | 55 | 7.24 | 41.6 | 8.2 | 70 | 35 | B |
| Barium (Ba) | mg/kg |  |  |  |  | 160 | 625 | 130.1 |  |  |  | 48 | A |
| Cadmium (Cd) | mg/kg | 0.38 | 1.4 | 1.5 | 10 | 0.8 | 12 | 0.68 | 4.21 | 1.2 | 9.6 | 3 | N |
| Chromium (Cr) | mg/kg | 49 | 141 | 80 | 370 | 0.38 | 220 | 52.3 | 160 | 81 | 37 | 62 | N |
| Cobalt (Co) | mg/kg |  |  |  |  | 2.4 | 180 |  |  |  |  | 10 | N |
| Copper (Cu) | mg/kg | 32 | 9.4 | 65 | 270 | 3.4 | 96 | 18.7 | 108 | 34 | 270 | 390 | M,O |
| Iron (Fe) | % |  |  |  |  |  |  |  |  |  |  | 22 | N |
| Lead (Pb) | mg/kg | 30 | 9.4 | 50 | 220 | 55 | 530 | 30.24 | 112 | 46.7 | 218 | 400 | B |
| Manganese (Mn) | mg/kg |  |  |  |  |  |  |  |  |  |  | 260 | N |
| Mercury (Hg) | mg/kg | 0.14 | 0.48 | 0.15 | 1 | 0.3 | 10 | 0.13 | 0.7 | 0.15 | 0.71 | 0.41 | M |
| Nickel (Ni) | mg/kg | 15 | 47 | 21 | 52 | 0.26 | 10 | 15.9 | 42.80 | 20.9 | 51.6 | 110 | E,L |
| Selenium (Se) | mg/kg |  |  |  |  | 0.7 | 100 |  |  |  |  | 1 | A |
| Silver (Ag) | mg/kg | 0.23 | 1.1 | 1 | 4 |  | 15 | 0.73 | 1.77 | 0.73 | 3.7 | 3.1 | A |
| Tin (Sn) | mg/kg |  |  |  |  | 19 | 900 | 0.05 |  |  |  | 3.4 | N |
| Vanadium (V) | mg/kg |  |  |  |  | 42 | 250 |  |  |  |  | 57 | N |
| Zinc (Zn) | mg/kg | 94 | 245 | 200 | 410 | 16 | 350 | 124 | 271 | 15 | 410 | 410 | I |

|  |  |
| --- | --- |
| 1 | T20/T50 = analyte conc. corresponding to 20 % & 50 % probability of toxicity for amphipods, as per [Field et al. 2002](https://doi.org/10.1002/etc.5620210929) |
| 2 | Default guideline value and guideline value – high = analyte concs. for low risk of toxic effects and potential commencement of toxic effects, respectively. From [Australian and New Zealand Guidelines for Fresh and Marine Water Quality, 2000.](https://www.waterquality.gov.au/anz-guidelines/resources/previous-guidelines/anzecc-armcanz-2000) |
| 3 | Target values = benchmark for environmental quality over longer term, assuming negligible risk for ecosystem; Intervention values indicate levels where functional properties of sediments for ecosystems is or will be seriously impaired. As per [Dutch Standards/Verbruggen et al., 2001](https://www.researchgate.net/publication/27452636_Ecotoxicological_Serious_Risk_Concentrations_for_soil_sediment_and_ground_water_updated_proposals_for_first_series_of_compounds) and [Buchman et al., 2008](https://repository.library.noaa.gov/view/noaa/9327) |
| 4 | TEL = Threshold Effect Level (or ISQG) and PEL = Probable Effect Level from [Canadian Sediment Quality Guidelines](https://ccme.ca/en/resources) developed by Canadian Council for Ministers of the Environment. Analyte conc. < TEL adverse effects rarely occur; analyte conc. >TEL but < PEL adverse effects occasionally occur; analyte conc. > PEL adverse effects frequently occur |
| 5 | ERL = Effect Range Low, defined as analyte conc. corresponding to 10% percentile of adverse effects and ERM = Effect Range Median, corresponding to 50% percentile of adverse effects, from [Long et al., 1995](https://doi.org/10.1007/BF02472006) |
| 6 | Apparent Effects Threshold = highest analyte concentration associated with a non-toxic sample, as per [Buchman et al., 2008](https://repository.library.noaa.gov/view/noaa/9327) |
| 7 | N = neanthes, E = echinoderm larvae, B = bivalve, A = amphipod, M = microbial ecotox, O = oyster larvae, E = echinoderm larvae, L = larval bioassay, I = infaunal community impacts, as per [Buchman et al., 2008](https://repository.library.noaa.gov/view/noaa/9327) |

International guidelines values for trace metals in US, Dutch, Australian, Canadian and British marine waters are defined below in Table A2.6. As with the marine sediments, the Dutch SRAeco represent analyte concentrations presenting a serious risk of environment harm and as such are not guideline upper limits but rather to be avoided at all costs.

**Table A2.6 International ecotoxicology guideline values for trace metals in seawater**

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | US EPA | | Dutch | | ANZ Guidelines | | | Canadian | | UK EQS | | Van Dam et al. (2008) |
| Analyte | Units | CCC1 | CMC1 | MPA2 | SRAeco2 | TOX LOSP 953 | TOX LOSP 903 | TOX LOSP 80/Unknown3 | Long term (chronic)4 | Short term (acute)4 | AA5 | MAC5 | 95% WQGV6 |
| Aluminium (Al) | µg/L |  |  |  |  |  |  |  |  |  |  | 1000# | 56 |
| Antimony (Sb) (III) | µg/L |  |  |  |  |  |  | 270 |  |  |  |  |  |
| Arsenic (As) | µg/L | 36 | 69 | 24 | 890 |  |  |  | 12.5 |  | 25 |  |  |
| Barium (Ba) | µg/L |  |  | 29FW | 7000FW |  |  |  |  |  |  |  |  |
| Beryllium (Be) | µg/L | 100\* |  |  |  |  |  |  |  |  |  |  |  |
| Boron (B) | µg/L |  |  |  |  |  |  |  | 1200BC |  | 7000 |  |  |
| Cadmium (Cd) | µg/L | 7.9 | 33 | 0.34 | 27 | 5.5 | 14 | 36 | 0.12 |  | 0.2 |  |  |
| Chromium (Cr) (III) | µg/L |  |  | 36FW | 220FW | 27 | 49 | 91 | 56 |  |  |  |  |
| Chromium (Cr) (VI) | µg/L | 50 | 1100 | 8.7 | 260 | 4.4 | 20 | 85 | 1.5 |  | 0.6 |  |  |
| Cobalt (Co) | µg/L |  |  | 3 | 810 | 1 | 14 | 150 |  |  | 3 |  |  |
| Copper (Cu) | µg/L | 3.1 | 4.8 | 1.1 | 18 | 1.3 | 3 | 8 | 2BC | 3BC |  |  |  |
| Gallium (Ga) | µg/L |  |  |  |  |  |  | 18 |  |  |  |  | 800 |
| Iron (Fe) | µg/L |  |  |  |  |  |  |  |  |  | 1000 |  |  |
| Lead (Pb) | µg/L | 8.1 | 210 | 11 | 150 | 4.4 | 6.6 | 12 | 2BC | 140BC | 1.3 | 14 |  |
| Manganese (Mn) | µg/L |  |  |  |  |  |  | 80 |  |  |  |  |  |
| Mercury (Hg) | µg/L | 0.94 | 1.8 | 0.23 | 2.7 | 0.4 | 0.7 | 1.4 | 0.016 |  |  | 0.07 |  |
| Molybdenum (Mo) | µg/L |  |  | 29 | 27000 |  |  | 23 |  |  |  |  | 3880 |
| Nickel (Ni) | µg/L | 8.2 | 74 | 1.9FW | 500FW | 70 | 200 | 560 |  |  | 8.6 | 34 |  |
| Phosphorus | µg/L |  | 0.1 |  |  |  |  |  |  |  |  |  |  |
| Selenium (Se) | µg/L | 71 | 290 |  |  |  |  |  |  |  |  |  |  |
| Silver (Ag) | µg/L |  | 0.95 |  |  | 1.4 | 1.8 | 2.6 | 1.5BC | 3BC | 2.6 | 0.5 |  |
| Thallium (Tl) | µg/L |  |  |  |  |  |  | 17 |  |  |  |  |  |
| Tin (Sn) | µg/L |  |  |  |  |  |  |  |  |  | 10 |  |  |
| Vanadium (V) | µg/L |  |  |  |  | 100 | 160 | 280 |  |  | 100 |  |  |
| Zinc (Zn) | µg/L | 81 | 90 | 7.3 | 89 | 8 | 12 | 21 | 10BC | 55BC | 6.8 |  |  |

|  |  |
| --- | --- |
| 1 | Criteria Chronic Concentration and Criteria Maximum Concentration, corresponding to 96-hour average and 1 hour average analyte concentrations - [US EPA recommended Water Quality Criteria for Aquatic Life - Marine](https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table). \* denotes threshold from National Academy of Sciences-National Academy of Engineering (NAS-NAE). 1972. Water Quality Criteria 1972. |
| 2 | Maximum Permitted Addition, based on added analyte concentration at which 95% of adverse effects on species or processes are avoided, and Serious Risk Addition for ecosystems, based on the added analyte concentration at which 50% of species or processes will experience adverse effects. As per [Dutch Standards/Verbruggen et al., 2001](https://www.researchgate.net/publication/27452636_Ecotoxicological_Serious_Risk_Concentrations_for_soil_sediment_and_ground_water_updated_proposals_for_first_series_of_compounds). FW shows thresholds from freshwater ecotox. data only, rather than combined freshwater/marine data |
| 3 | Default guideline values for analyte concentrations corresponding to Toxicant Limit of Species Protection (LOSP) for 95%, 90% and 80% or unknown level of species protection, as per [Australia and New Zealand Guidelines for Fresh and Marine Water Quality](https://www.waterquality.gov.au/anz-guidelines/), revised 2018. |
| 4 | Long term (chronic) and short term (acute) [Canadian Marine Quality Guidelines](https://ccme.ca/en/summary-table) developed by Canadian Council for Ministers of the Environment (CCME). Where CCME guidelines are absent, [Ambient Water Quality Guidelines (AWQG)](https://www2.gov.bc.ca/gov/content/environment/air-land-water/water/water-quality/water-quality-guidelines/approved-water-quality-guidelines) from the British Columbia Ministry of Environment and Climate Change are used and are denoted by BC |
| 5 | Annual Average and Maximum Allowable Concentration Environmental Quality Standards from UK Environment Agency [Surface Water Pollution Risk Assessment](https://www.gov.uk/guidance/surface-water-pollution-risk-assessment-for-your-environmental-permit). # only if pH ≥6. If effluent dilution > 10, emissions standard of 10,000 µg/L dissolved applies |
| 6 | Van Dam et al., 2018. Water quality guideline values for aluminium, gallium and molybdenum in marine environments <https://doi.org/10.1007/s11356-018-2702-y> |

## A2.3 Impact of dilution in wastewater discharge and receiving waters

When evaluating the potential environmental impacts of OAE using Planetary’s method of alkalinity addition to existing wastewater discharge, the dilution of the alkalinity in both i) the wastewater effluent and ii) the receiving waters must be considered. The critical consideration is whether the ambient environmental conditions in the receiving waters are significantly deleteriously affected by the alkalinity addition. The effects of alkalinity addition must therefore be screened against the identified guideline values described in previous sections once dilution in the wastewater discharge and the receiving waters has been accounted for. This approach is borne out by regulatory guidance, such as the screening workflow for risk assessment of surface water pollution in discharges to estuarine and coastal waters defined by the UK Environment Agency. The published guidance outlines a sequential series of screening tests to assess the risk of deleterious impacts upon the environment, once dilution has been factored in (summary of assessment in Table A2.7). The final step of the screening workflow is to conduct modelling work to determine whether EQS limits are met once dilution has been factored in, and to characterize the mixing zone formed as the discharge disperses into the receiving waters.

**Table A2.7 Screening workflow for surface water pollution risk assessment of discharge in the UK**

|  |  |
| --- | --- |
| Test | Description |
| Simple screening against EQS limits | The levels of pollutants in the discharge are screened against Annual Average and Maximum Allowable Concentration EQS limits set out in the Estuarine and Coastal Waters Specific Pollutants and Operational Environmental Quality Standards list and the Estuarine and Coastal Waters Priority Hazardous Substances list. |
| Low water channel/estuarine discharge | Is the discharge to the low water channel in the upper parts of an estuary, where the receiving water is mainly fresh? |
| Reduced dilution/dispersion | Is the discharge to a location with restricted dilution or dispersion? |
| Distance of discharge point offshore | Is the discharge less than 50 m offshore from where the seabed is at chart datum and/or is the seabed at the discharge location less than 1 m below chart datum? |
| Effective volume flux (for buoyant discharges only) | The screening test for buoyant discharges consists of calculating the effective volume flux for each of the pollutants screened and then comparing this against the maximum allowable effective volume flux, which varies depending on the depth of the discharge location. For receiving waters of greater than 3.5 m below chart datum, the maximum allowable effective volume flux is fixed at 3.5 m3 per second. |
| Additional Test: Priority Hazardous Pollutants | Additional screening for substances listed on the Priority Hazardous Substances List. Calculate the cumulative annual load of any PHS substances identified in the discharge to derive a figure in kg per year. These figures are compared against fixed limits. |
| Modelling | If concentrations of identified pollutants in the discharge do not pass any of the above screening tests, modelling work should be carried out.  The objective of modelling work is to ascertain if the EQS limits are met after dilution and to characterize the mixing zone from the discharge, taking into account background concentrations of pollutants. If the EQS limits are met then the substances are not liable to cause pollution, and need no further assessment.  It is recommended that graphical representations of the mixing zones resulting from hydrodynamic models are interpreted alongside spatial data showing identified environmental sensitivities around the discharge location. |
|  | |

## A2.4 Ecological Safety of OAE in peer-reviewed literature

Whilst the environmental impacts of ocean acidification (OA) have been the focus of considerable scrutiny, the environmental effects of ocean alkalinity enhancement are comparatively less well understood (Bach et al., 2019; Burt et al., 2021; Gately et al., 2023). This is unsurprising given that more widespread academic attention to OAE only began in recent years. To date, the bulk of these studies have focused on phytoplankton communities, and results generally show that impacts on these critical communities is neutral or minimal, particularly at alkalinity addition scenarios that are relevant for early field studies. Consensus from these researchers is that more work is needed, and with dedicated funding now shifting towards this effort, we anticipate a rapid acceleration in our learning over the coming years.

Renforth & Henderson (2017) highlight the extensive research that has been conducted to investigate the impact of OA on marine biota by experimentally increasing pCO2 and/or decreasing pH and carbonate saturation state (Ω), but note that there are few studies investigating the impact of reversing OA or elevating TA on marine biota. The wealth of OA research to date has been key to guiding and informing research into the impacts of OAE (Iglesias-Rodríguez et al., 2023; Subhas et al., 2023), and there is general agreement in the scientific literature that dedicated research is needed on the risks and possible impacts of deploying OAE at scale, with a number of authors outlining potential risks and knowledge gaps for further research (e.g., Renforth et al., 2019). As well as laboratory and mesocosm experiments, Cyronak et al. (2023) note that real world trials into OAE offer a number of advantages, including observing natural ecological and ecosystem dynamics/impacts, understanding the role of natural biogeochemical cycles and physical processes, and assessing scalability.

Alongside consideration of potential deleterious impacts and risks, a number of studies have focused on the environmental co-benefits of OAE, such as the potential to protect coral reef ecosystems (Albright et al., 2016; Mongin et al. 2021; Vakilifard et al., 2021) and to locally mitigate against OA. As well as outlining the benefits of delivering alkalinity to coastal environments through existing wastewater discharges, as per the Planetary approach, Cai and Jiao (2022) highlight the sensitivity of coastal regions, and recommend that impacts on environments, organisms, and ecosystems be carefully evaluated, as coastal zones already face multiple environmental and climate-related stressors and are typically more vulnerable than the open ocean. However, the authors also note that existing wastewater discharge – which is typically low pH and high-DIC relative to seawater – represents an important source of DIC and acidification in coastal environments which may already be deleteriously affecting coastal ecosystems, and which could be mitigated by OAE. Overall, Cai and Jiao posit that the likely environmental, biological, and ecosystem impacts required to deliver OAE at a meaningful scale are expected to be small, given the minimal modification of carbonate chemistry required and the scale of the systems involved.

One key risk area identified for OAE has been the potential deleterious environmental impact not of the alkalinity itself but rather any dissolution co-products present in the source material (Renforth et al., 2019; Cyronak et al., 2023). These impurities may include potentially beneficial nutrients for nutrient-limited systems, such as silicates, iron and magnesium (Hartman et al., 2013), but there is also concern about the presence of trace metal impurities, such as nickel (Montserrat et al., 2017; Guo et al., 2022). In a study investigating the impacts of nickel on the growth and photo-physiological response of 11 phytoplankton species, Guo et al. (2022) found that, in general, the organisms studied were not especially sensitive to Ni concentrations but that there was inter-specific variation, with cyanobacteria and one dinoflagellate taxon exhibiting greater sensitivity. The authors’ overall conclusions were that excess Ni had a limited toxic impact on most phytoplankton species included in the study and, given that the study organisms selected encompassed considerable taxonomic diversity, the results could be generalised more widely across temperate phytoplankton (Guo et al., 2022). They did, however, caveat the results by noting that they used a chelating ligand known as EDTA during experimentation, which may have bound to much of the total Ni recorded and hence reduced the reactive, available quantity which could have caused a toxic effect on the study organisms.

In another recent laboratory study, the impacts of olivine leachates (containing Si, Ni, Mg, Fe, Cr, and Co) upon six species of phytoplankton were assessed (Hutchins et al., 2023). The study organisms comprised two silicifying diatoms, a calcifying coccolithophore and three cyanobacteria, and the overall conclusions were that all groups displayed either positive or neutral physiological effects in response to all treatments in the short term. The authors did note some variation between groups, with silicifiers benefitting from iron and silicate whilst calcifiers benefitted from enhanced alkalinity. Other trace metals, such as nickel and cobalt, also supported cyanobacterial growth (Hutchins et al., 2023). In a modelling study on the effects of olivine dissolution on phytoplankton, Kohler and colleagues (2013) posit a possible phytoplankton community shift towards silicifying diatoms as a consequence of silicic acid inputs, which could impact the biological carbon pump (also discussed in Bach et al., 2019; Fakhraee et al., 2022; Ferderer et al., 2022). The potential for trace metal inputs (such as Fe or Ni) to cause phytoplankton community shifts, in a process somewhat analogous to ocean fertilization, has also been discussed (Kohler et al., 2013; Hartmann et al., 2013). That said, these studies are based on extrapolations of modelling work which have been scaled up to a level of OAE necessary to deliver planetary-scale CDR, and the authors recognize that these forecasts are not yet borne out by real world evidence.

The potential impacts of OAE on microbial communities were also considered in a study by Subhas et al. (2022), which examined microbial responses to alkalinity perturbations in the North Atlantic subtropical gyre, using mesocosm experiments onboard a research vessel. Microbial communities demonstrated occasionally measurable but mostly negligible responses to alkalinity enhancement, even at extreme alkalinity perturbations of 2000 µmol kg-1, although there were some reductions in primary production and a shift towards smaller microbial particle size classes following OAE treatment for stations located in the centre of the gyre (but not for stations at the gyre periphery). The authors advocate further studies into the impacts of OAE in diverse marine environments (Subhas et al., 2023).

The physical impacts of OAE have also been flagged; Montserrat et al., (2017) have called for research into the potential for increased suspended particulate matter, sediment pore space clogging and smothering risk when considering olivine distribution in coastal ecosystems. Bach et al. (2019) flag the physical impact on marine ecosystems from the addition of large amounts of finely ground material, which could elevate turbidity following its initial addition or during subsequent resuspension, or induce secondary precipitation of particulates from the water column. Subhas et al. (2023) note that current scientific understanding is limited on how the sustained, large-scale addition of particles linked to OAE might influence seawater turbidity, flocculation, particle settling velocities and the marine ecosystem at multiple levels, whilst Kohler et al. (2013) have considered the risk of a reduction in light transmission through the water column in response to olivine dissolution.

In terms of the risk presented to marine ecosystems from the OAE-induced alkalinity perturbation itself, phytoplankton are probably the most studied group. Ferderer et al. (2022) studied the effects of alkalinity addition of c. 500 µmol kg-1 on the growth and biomass of 5 different groups of phytoplankton and on heterotrophic bacteria, and found that simulated OAE had significant but generally moderate effects on the various groups. The experiment simulated OAE with both equilibrated and unequilibrated treatments, which were intended to simulate conditions with and without the effects of air-sea gas exchange included, respectively. Of interest was that the unequilibrated treatment did not have a noticeably larger impact on the phytoplankton (and heterotrophic bacteria) community than the equilibrated treatment, even though the changes in carbonate chemistry conditions were much more severe. Overall, the authors concluded that the inadvertent effects of increased alkalinity on the coastal phytoplankton communities appear to be rather limited relative to the enormous climatic benefit of increasing the ocean’s inorganic carbon inventory (Ferderer et al., 2022.).

Gately et al., (2023) conducted a similar experiment to investigate the impacts of moderate (~700 μmol kg-1) and high (~2700 μmol kg-1) alkalinity addition on the growth rate and elemental ratios of two groups of phytoplankton: a silicifying diatom and a calcifying coccolithophore. Both groups showed a neutral response to alkalization at both treatment levels, although some abiotic mineral precipitation occurred. The results of both Ferderer et al. (2022) and Gateley et al. (2023) are summarized in Table A2.8.

**Table A2.8 Alkalinity perturbations and impacts on various phytoplanktonic groups and bacteria**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Species/group | | Functional  Group | Alkalinity perturbation  (µmol/kg) | TA Source | Impacts Assessed | Outcomes relative to control |
| *Emiliana huxleyi* | | Coccolithophores (calcifiers), phytoplankton | 700 | Na2CO3 + CaCl2.H2O | Growth, elemental ratios | Undetectable1 |
| 2700 |
| *Chaetoceros* sp. | | Diatoms (silicifiers), phytoplankton | 700 |
| 2700 |
| Synechococcus | | Cyanobacteria, phytoplankton | 495 | NaOH | Growth | Slightly reduced bloom & faster decline2 |
| 501 | NaOH + NaHCO3 |
| 495 | NaOH | Biomass | Later bloom decline2 |
| 501 | NaOH + NaHCO3 | Earlier bloom decline2 |
| Picoeukaryotes | | Phytoplankton | 495 | NaOH | Growth | Reduced & delayed bloom 2 |
| 501 | NaOH + NaHCO3 | Undetectable2 |
| 495 | NaOH | Biomass | Reduced bloom2 |
| 501 | NaOH + NaHCO3 | Undetectable2 |
| Cryptophytes | | Phytoplankton | 495 | NaOH | Growth | Reduced & delayed bloom2 |
| 501 | NaOH + NaHCO3 |
| 495 | NaOH | Biomass | Undetectable2 |
| 501 | NaOH + NaHCO3 |
| Nanophytoplankon | | Phytoplankton | 495 | NaOH | Growth | Greater post-bloom count2 |
| 501 | NaOH + NaHCO3 | Undetectable2 |
| 495 | NaOH | Biomass | Slightly greater2 |
| 501 | NaOH + NaHCO3 |
| Microphytoplankton | | Phytoplankton | 495 | NaOH | Growth | Undetectable2 |
| 501 | NaOH + NaHCO3 |
| 495 | NaOH | Biomass |
| 501 | NaOH + NaHCO3 |
| Heterotrophic bacteria | | Bacterioplankton | 495 | NaOH | Growth | Earlier bloom2 |
| 501 | NaOH + NaHCO3 |
| 1 | Coccolithophores and diatoms resilient to ocean alkalinity enhancement: A glimpse of hope? Science advances, 9(24), eadg6066. https://doi.org/10.1126/sciadv.adg6066 | | | | | |
| 2 | Ferderer, A., Chase, Z., Kennedy, F., Schulz, K. G., and Bach, L. T.: Assessing the influence of ocean alkalinity enhancement on a coastal phytoplankton community, Biogeosciences, 19, 5375–5399, https://doi.org/10.5194/bg-19-5375-2022, 2022. | | | | | |

A number of studies have also investigated the effects of elevated alkalinity on other organisms. Cripps et al. (2013) investigated the biological impacts of elevated alkalinity on the European green crab *Carcinus maenas* with acute exposure to Ca(OH)2 treatments of 0.28 and 0.54 mmol L-1, intended to simulate the level of alkalinity addition that might be required to reverse the decline in ocean surface pH since the pre-industrial era. The results indicated that the acid-base balance of the individuals was slightly affected, with the greatest effect noted in mature females. The authors do note, however, that a lessor alkalinity perturbation sufficient to counteract the effects of carbonate decline only rather than reverse pH to pre-industrial levels (i.e., a much smaller concentration of alkalinity) might not lead to detectable impacts (Cripps et al., 2013).

Gore et al. (2019) considered the effects of elevated TA on a benthic calcifying macroalgae (*Corallina* sp.) through the addition of 0.5 mol L-1 Na2CO3 and noted that increased TA did not significantly influence Corallina sp. primary productivity, respiration, or photophysiology relative to a control. The authors concluded that, whilst further research is needed, OAE might be not intrinsically detrimental for *Corallina* sp., and furthermore that is has potential to mitigate the deleterious effects of ocean acidification on this taxon, as enhanced calcification rates were recorded in the experimental organisms following alkalinity treatment. In further work, the response of the calcifying phytoplankton *Synechococcus* 8806 to elevated TA was also assessed (Gore, 2021); results indicated greater growth and higher rates of biological CaCO3 precipitation following alkalinity treatment, which suggest that OAE is also unlikely to be intrinsically detrimental for this phytoplankton taxon.

## A2.5 Ecological monitoring for OAE - Identification of targets and impacts

The first step in designing an appropriate monitoring programme is identification of sensitive receptors in the marine environment, together with the adverse impacts they might experience from alkalinity addition.

Iglesias-Rodríguez et al. (2023) note that, when considering those organisms most likely to be affected by OAE, special attention should be paid to those species that (1) significantly impact or respond biogeochemically to chemical changes caused by alkalinity addition (e.g., possibly calcifiers, photosynthetic organisms); (2) keystone organisms (e.g., corals, toxin-producing phytoplankton); and (3) organisms/functional groups of known vulnerability to climate change (corals, sea urchins).

The following is a general and non-exhaustive list of receptors; it should be noted that these represent a core list and that additional receptors may need to be considered on a site-by-site basis.

* Benthic epifauna (invertebrates) and epiflora (algae)
* Benthic infauna
* Benthic microbial communities
* Phytoplankton
* Zooplankton, including larvae of fish and invertebrates
* Fish & shellfish
* Avifauna
* Higher trophic level organisms, such as marine mammals (cetaceans and pinnipeds)

At the most fundamental level, alkalinity addition to coastal environments could affect the physical and chemical properties of the water column and/or the marine sediments. Whilst these impacts may then interact with the biological receptors identified above through a variety of mechanisms, the root causes of all impacts should be traceable back to alteration of one or both of these sets of properties. The following is a list of some of the potential impacts which have been identified and considered:

**Physical Perturbations**

* Undissolved particles of mineral added alkalinity – magnesium hydroxide – accumulate on seabed around alkalinity addition point, resulting in physical impacts to benthic environment and concomitant impacts upon benthic ecosystems.
* Added alkalinity particles lead to an increase in total suspended solids (and hence turbidity). This can have two differing impacts: 1) reducing the natural light penetration through the water column and impacting primary productivity of both pelagic and benthic photosynthesisers, and/or 2) particle ingestion by biota.
* Physical properties of the water are modified, such as increased density as a result of dissolved alkalinity.

**Chemical Perturbations**

* Reduction in aqueous CO2 around the addition point, which impacts photosynthesising primary producers (phytoplankton/algae).
* Changes in ambient water quality (pH, alkalinity) affect zooplankton, including survival and recruitment of commercially important shellfish or finfish larvae.
* Addition of alkaline substances to seawater causing localized increase in salinity, which could have negative impacts on marine organisms that are hypersensitive to salinity fluctuations.
* Changes in the carbonate chemistry of seawater around the addition point, which could impact marine ecosystems and biogeochemical cycles, such as the cycling of carbon, oxygen, and nutrients.
* Disturbance to the natural concentrations of macro- or micronutrients through dissolution by-products.
* Reduction in water or sediment quality around the addition point due to the presence of trace metal impurities present as dissolution by-products in the added alkalinity.

When considering how the above chemical and physical perturbations might affect biological receptors, the following considerations are cited by Cyronak et al. (2023) in a best practice guide to conducting OAE field trials:

* What organisms (benthic and pelagic) are present in the project area and what are their relative sensitivities to fluctuations in seawater carbonate chemistry (if known)?
* Are there endangered or rare species present? Is the site a nursery and/or nesting ground? Are there keystone species and/or important primary producers present?
* What are the trophic dynamics in the environment, and how might the food web be impacted (e.g., shifts in predator/prey relationships)? What are the cascading implications for the ecosystem as a whole? Might effects be transferred beyond the study site via migratory species?
* Could particulates (e.g., ground rock) cause physical damage prior to dissolution?

Development of an effective ecological monitoring plan will require due consideration of these perturbations and potential receptor impacts.

The listed biological receptors encompass a wide range of trophic levels, from the bottom of the food web (phytoplankton and microbes) to the top (marine mammals). Any direct impacts arising from alkalinity addition will be most easily detected in lower trophic level organisms, as a result of shorter generation times and increased sensitivity to physical or chemical changes to the water and sediment, which are the mechanisms by which biota would be affected by alkalinity addition. As such, in order to maximize the possibility of detecting any impact, it is reasonable that a monitoring programme should be primarily aimed at water and sediment quality together with lower trophic level organisms. This does not mean that higher trophic level organisms should be excluded from the scope; in fact, these organisms depend upon primary producers at the base of the food web and are most likely to be impacted by second-order effects, such as disruption to lower trophic level organisms resulting in the altered availability of prey species. Closely monitoring the base of the food web alongside water quality metrics (e.g., suspended solids and trace metals) will help understand whether any risk exists to higher trophic level animals that ingest water, particles, or lower trophic level organisms. In other words, by monitoring water quality and lower trophic levels, a monitoring programme will provide a signal as to any potential cascading second-order impacts upon organisms higher in the food web.

Direct impacts upon higher trophic level organisms such as marine mammals are not considered likely, given that natural spatial and temporal variation in seawater properties (pH, DIC, TA) across the ranges of these species and across seasons greatly exceed any differences that will arise at the proposed addition rates (Howland et al., 2000; Humphreys et al., 2020; Kitidis et al., 2012).

## A2.6 References

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# Appendix 3; OAE related acronyms and glossary

η (Greek eta) fraction of CDRMAX that is realized in the ocean

σ (Greek sigma) standard deviation; σ2 variance.

ALK CO2-reactive alkalinity (tonnes)

CDR Carbon dioxide removal

CDRCRED Creditable CDR quantity (tCO2) after deduction of holdback

CDRGROSS CDR achieved in the ocean before accounting for life-cycle emissions

CDRMAX Maximum CDR achievable for a given quantity of alkalinity added to seawater

CDRNET Net CDR after deduction of LCA emissions (ELCA) from CDRREM

[CO2] CO2 concentration

CO2e CO2 equivalents

[CO32-] Carbonate ion concentration

DIC Dissolved inorganic carbon

ECHA European Chemicals Agency

EC50 Half maximal effective concentration

ELCA Life-cycle emissions (tCO2e) associated with a given CDRREM quantity

EW Enhanced weathering

GHG Greenhouse gas

GMST Global mean surface temperature

GtCO2 Gigaton CO2 (109 metric tonnes = 1012 kg)

[H+] Hydrogen ion concentration (10-pH)

[HCO3−] Bicarbonate ion concentration

HSE Health, safety, and environment (also SHE or HE)

LC50 Median lethal dose

LCA Life cycle analysis

LCIA Life cycle impact assessment

mCDR Marine carbon dioxide removal

MODOM Modular dosing and monitoring system

MtCO2 Megaton CO2 (106 metric tonnes = 109 kg)

MW Molecular weight

NET Negative emissions technology

NOEC No observed effect concentration

NTU Nephelometric turbidity units

OA Ocean acidification

OAE Ocean alkalinity enhancement

pCO2 Partial pressure of CO2

PIC Particulate inorganic carbon

POC Particulate organic carbon

ppb parts per billion

ppm parts per million

ppt parts per thousand

RAM Risk assessment matrix

S Seawater salinity

SOCEAN Ocean sink, the annual, global air-sea CO2 flux ((ca. 3 GtC/yr)

SSR (GHG) sources, sinks, and reservoirs

SST Sea surface temperature

T Temperature

TA Total alkalinity

TDS Total dissolved solids

TRL Technology readiness level

TSS Total suspended solids

VOI Value of information

## OAE related glossary

*Carbonate buffering*

Carbonate buffering is the geochemical process that stabilizes the ocean’s pH, limiting the acidification impact of the CO2 uptake as a result of increasing atmospheric [CO2]. If ocean pH drops as a result of CO2 uptake, carbonate ions will recombine with H+, reducing [H+] and stabilizing pH. With sufficient carbonate (CO32-) ions present, the ocean pH change as a result of CO2 dissolution is thereby reduced. As [CO32-] is reduced by this process, further CO2 addition will result in increasing acidification. Conversely, an increase in ocean pH favors the conversion of carbonic acid (H2CO3) to bicarbonate (HCO3−) and subsequently to carbonate ions, resulting in the release of H+ and limiting the rise in pH.

*Dissolved inorganic carbon*

Dissolved inorganic carbon (DIC) is the sum of all inorganic carbon species in seawater. DIC is distributed between dissolved CO2 plus carbonic acid (together denoted H2CO3\*), bicarbonate (HCO3-), and carbonate (CO32-) ions, in proportions that depend on the seawater pH (see *Carbonate buffering*). The average DIC in the world’s oceans is around 2000 µmol/kg.

*Eddy covariance measurement*

Eddy covariance is a technique for determining the vertical flux of a gases by statistical analysis of the vertical velocity and fluctuating concentration of turbulent eddies, and is used to assess the air-sea CO2 gas exchange velocity.

*Environmental footprint*

The environmental footprint of a product (or service) is a measure of its life-cycle environmental performance, established through a multi-issue life-cycle impact assessment. It complements the carbon footprint, assessed using a life-cycle assessment of GHG emissions.

*Heterotroph*

Heterotrophs are organisms that obtain organic carbon by feeding on autotrophs—organisms that produce organic compounds directly from inorganic carbon—or on other heterotrophs. Marine autotrophs include algae and other phytoplankton, which use photosynthesis to produce organic substrates, while zooplankton, which feed on phytoplankton or other zooplankton are heterotrophs. Ingestion of alkaline mineral particles by heterotrophic organisms would result in a (temporary?) reduction in the efficiency of OAE by mineral addition.

*Keystone species*

A species that, relative to its abundance, has a disproportionate effect on its natural environment, playing a key role in maintaining the ecological community structure through its impact on other organisms in an ecosystem.

*Mixed layer*

The upper layer of the ocean that is mixed and homogenized by turbulent eddies carrying the energy from wind and wave action down from the surface. The mixed layer depth (MLD) is shallowest in the summer, due to lower windspeeds and higher sea surface temperature, and deepest in the winter. A number of different thresholds have been used to define the MLD, of which the most common is a density increase of 0.03 kg/m3 from surface conditions[[48]](#footnote-48).

*Nephelometric turbidity unit*

Nephelometric turbidity unit (NTU) is the standard unit of turbidity used in environmental monitoring in the United States and is determined by comparing the intensity of white light scattered at an angle of 90 degrees from the incident bean in a test sample against a reference solution. The international standard unit is the Formazin nephelometric unit (FNU) which is measured in the same way except that an infrared source is used.

*Pycnocline*

The pycnocline is the zone near the ocean surface in which the density gradient is maximum, separating a surface layer of warmer, less dense water from colder, denser waters below.

*Specific area*

The total surface area of a material per unit mass (m2/gm). The rate of dissolution and of chemical reactions that take place on particle surfaces increases with the specific area of a material, for example as a result of grinding or milling into smaller particles.

*Stratification*

Stratification occurs when ocean waters of differing salinity and temperature form a stable layering, with less dense layers (warm/fresher) above denser layers (colder/more saline). Stratification impedes the vertical mixing of surface waters that aids the oxygenation of deeper waters and the recycling of nutrients into the well-lit (euphotic) zone.

*Thermocline*

The thermocline is the boundary layer separating warmer surface ocean water (the epilimnion) from colder deeper water (the hypolimnion). On a small scale this can be experienced when swimming in the sea on a warm summer day and, in tropical seas, the water temperature can drop from 25°C at the surface to ca. 10°C below the thermocline, at 100 - 200 m water depth.



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