Salinity from space unlocks satellite-based assessment of ocean acidification

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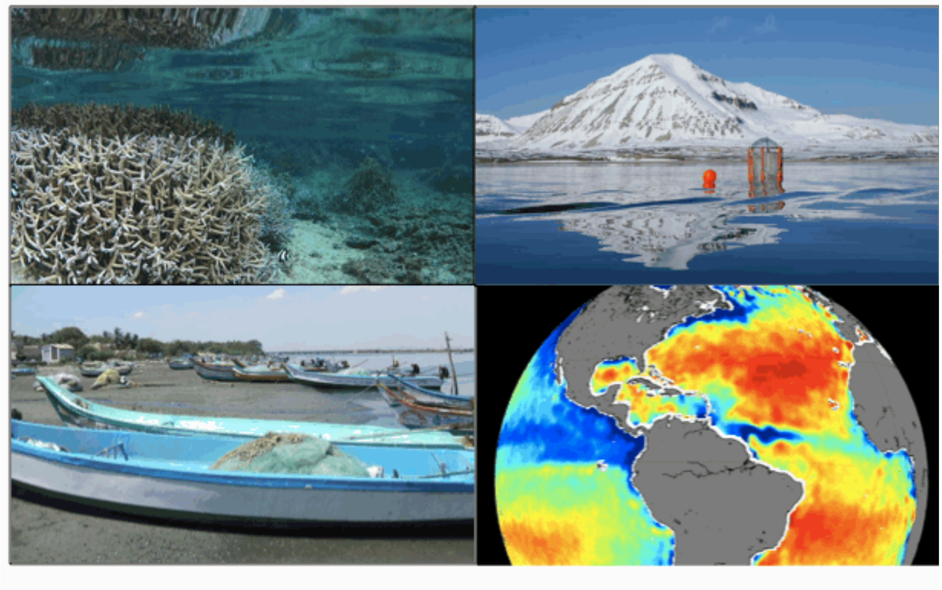

Abstract artwork

Note to editor (top left to bottom right): Tropical coral; Svalbard in the Barents Sea; Beach in India on the coast of the Bay of Bengal; Salinity from space (SMOS) showing the Amazon plume. All images taken by PML staff and used with permission.

Approximately a quarter of the carbon dioxide (CO_2) that we emit into the atmosphere is absorbed by the ocean. This oceanic uptake of CO_2 leads to a change in marine carbonate chemistry resulting in a decrease of seawater pH and carbonate ion concentration, a process commonly called 'Ocean Acidification'. Salinity data are key for assessing the marine carbonate system, and new space-based salinity measurements will enable the development of novel space-based ocean acidification assessment. Recent studies have highlighted the need to develop new *in situ* technology for monitoring ocean acidification, but the potential capabilities of space-based measurements remain largely untapped. Routine measurements from space can provide quasi-synoptic, reproducible data for investigating processes on global scales; they may also be the most efficient way to monitor the ocean surface. As the carbon cycle is dominantly controlled by the balance between the biological and solubility carbon pumps, innovative methods to exploit existing satellite sea surface temperature and ocean color, and new satellite sea surface salinity measurements, are needed and will enable frequent assessment of ocean acidification parameters over large spatial scales.

1. Introduction

Each year global emissions of carbon dioxide (CO_2) into our atmosphere continue to rise. These increasing atmospheric concentrations cause a net influx of CO_2 into the oceans. Of the roughly 36 billion metric tons of CO_2 that is emitted into our atmosphere each year, approximately a quarter transfers into the oceans [1]. This CO_2 addition has caused a shift in the seawater carbonate system, termed Ocean Acidification (OA), resulting in a 26% increase in acidity and a 16% decrease in carbonate ion concentration since the industrial revolution [2]. Recently there has been recognition that this acidification is not occurring uniformly across the global oceans, with some regions acidifying faster than others [3, 4]. However, the overall cause of OA remains consistent: the addition of CO_2 into the oceans, and as such, it remains a global issue. Continual emissions of CO_2 into the atmosphere over the next century will decrease average surface ocean pH to levels which will be deleterious to many marine ecosystems and the services they provide [5].

While the seawater carbonate system is relatively complex, two parameters have been suggested as pertinent to the monitoring and assessment of OA through time and space. These are pH (the measure of acidity) and calcium carbonate ($CaCO_3$) mineral saturation state, with aragonite generally considered to be an important $CaCO_3$ mineral to be monitored because of its relevance to marine organisms (e.g. corals) and its relative solubility. Thermodynamically, $CaCO_3$ is stable when the saturation state (an index of the concentrations of calcium and carbonate ions) is greater than one and becomes unstable when seawater becomes undersaturated with these ions (saturation < 1). While there is significant variability between types of organism, there is ample experimental evidence that many calcifying organisms are sensitive to OA [6], and that thresholds exist below which some organisms become stressed and their well-being and existence becomes threatened [7]. Increasingly evidence suggests that the physiology and behaviour of calcifying and non-calcifying organisms can be impacted by increasing OA [8], with cascading effects on the food chain and protein supply for humans [3], and alterations to the functioning of ecosystems and feedbacks to our climate [9].

In 2012 the Global Ocean Acidification Observing Network (GOA-ON, www.goa-on.org) was formed in an attempt to bring together expertise, datasets and resources to improve OA monitoring. At present, OA monitoring efforts are dominated by *in situ* observations from moorings, ships and associated platforms. Whilst key to any monitoring campaign, *in situ* data tend to be spatially sparse, especially in inhospitable regions, and so on their own are unlikely to provide a comprehensive, robust and cost effective solution to global OA monitoring. The need to monitor and study large areas of the Earth has driven the development of satellite-based sensors.

Increasingly, as *in situ* data accumulate, attempts are being made to use *in situ* hydrographic data [10-13] and/or remotely-sensed data [14, 15] to provide proxies and indicators for the condition of the carbonate system, enabling data gaps to be filled in both space and time. The increased availability of *in situ* data creates a substantial dataset to develop and test the capabilities of satellite-derived products, and we suggest that the recent availability of satellite-based salinity measurements provides new key insights for studying and assessing OA from space.

2. The complexities of the carbonate system

The oceanic carbonate system can be understood and probed through four key parameters: total alkalinity (TA), dissolved inorganic carbon (DIC), pH and fugacity of CO_2 (f_{CO2}). The latter may be replaced with the related partial pressure of CO_2, p_{CO2}, from which f_{CO2} can be calculated, and the two are often used interchangeably. In principle, knowledge of any two of these four is sufficient to solve the carbonate system equations. However, over-determination, the process of measuring at least three parameters, is advantageous.

The relationships between the different carbonate system parameters are fundamentally driven by thermodynamics, hence influenced by temperature and pressure, and knowing these is fundamental for calculating the carbonate system as a whole [16]. Water temperature is the major controller of the solubility of CO_2 [17], so seasonal changes in sea temperature can, depending on the region, be significant for driving changes in f_{CO2} (and consequently DIC and pH). Salinity affects the coefficients of the carbonate system equations. Hence to solve the equations, it is necessary to estimate temperature, salinity and pressure along with carbonate parameters.

The ratio between ions (the constituents of salinity) will tend to remain constant anywhere in the global oceans, resulting in a strong relationship between TA and salinity [18]. Unfortunately, a universal relationship between TA and salinity does not apply in certain regions, for instance in areas influenced by freshwater outflows from rivers [7], or areas where calcification and/or $CaCO_3$ dissolution occurs, such as where calcifying plankton are prevalent [19]. In these regions, it is therefore critical to gain additional local knowledge. For example, different rivers will have different ionic concentrations (and therefore different TA concentrations) depending on the surrounding geology and hydrology.

For DIC, f_{CO2} (or p_{CO2}) and pH, the other important process is biological activity [19]. Removal or addition of CO_2 by plankton photosynthesis or respiration can be a significant component of the seasonal signal [20]. Biological activity, in turn, is driven by factors such as nutrient dynamics and light conditions, which again are regionally specific. Measurements of chlorophyll (a proxy for biomass) and/or oxygen concentration can be useful for interpreting the biological component of the carbon signal.

The combination of these processes means that it is extremely challenging to produce a global relationship between any component of the carbonate system and its drivers. To enable us to understand these dynamics, extrapolation from collected data points to the global ocean is needed, and along with model predictions, empirical relationships and datasets are important and need to be studied and developed. OA needs to be assessed using these relationships on a global scale, but regional complexities, particularly where riverine and coastal processes dominate [21, 22], cause significant challenges for global empirical relationships.

3. Current *in situ* approaches and challenges

Laboratory measurements are the gold standard for assessing the carbonate system in seawater, with accuracy far in excess of that achievable from satellites.[23-25] However, research vessel time is expensive and limited in coverage, so autonomous *in situ* instruments are also deployed, e.g. on buoys, with less accuracy [26]. A notable example is the Argo network of over 3000 drifters, which measure temperature and salinity throughout the deep global ocean. Interpolation of Argo data is much less challenging than for most *in situ* measurements. Argo is the closest *in situ* data have come to the global, synoptic measurements possible with satellites, but shallow or enclosed seas are not represented (there are as yet no Argo instruments in the open Arctic Ocean). Table 1 lists more examples. Of the four key parameters, only f_{CO2} (or p_{CO2}) and pH are routinely monitored *in situ*. As yet there are limited capabilities to measure DIC and TA autonomously, hence these parameters must be measured either in a ship-based laboratory or on land.

Dataset name and reference	**Temporal period**	**Geographic location**	**Variables**	**No. of data points**
SOCAT v2.0[27]	1968-2011	Global*	fCO_2, SSS, SST	6,000,000+
LDEO v2012[28]	1980-present	Global*	pCO_2, SSS, SST	6,000,000+
GLODAP[29]	1970-2000	Global	TA, DIC, SSS, SST, Nitrate	10,000+

CARINA AMS v1.2[30]	1980-2006	Arctic	TA, DIC, SSS, SST	1500+
CARINA ATL v1.0[31]		Atlantic		
CARINA SO v1.1[32]		Southern Ocean		
AMT[33]	1995-present	Atlantic	pCO_{2W}, SSS, SST, Chl, pH	1000+
NIVA Ferrybox[34]	2008-present	Arctic	pCO_{2W}, TA, DIC, SSS, SST	1000+
OWS Mike[35]	1948-2009	Arctic	TA, DIC, SSS, SST, Chl	1000+
RAMA Moored buoy array[36]	2007-present	Bay of Bengal	SSS, SST	1000+
ARGO buoys[37]	2003-present	Global	SSS, SST	1,000,000+
OOI[38]	2014 onwards	Global (6 sites)	pCO_2, SSS, SST, nitrate	New program
SOCCOM[39]	2014 onwards	Southern Ocean	SSS, SST, pH, nitrate	New program

Table 1. *In situ* datasets and programs than can be used for the development and validation of OA remote sensing algorithms.

4. Potential of space based observations

4.1 Advantages and disadvantages

While it has proven difficult to use remote sensing to directly monitor and detect changes in seawater pH and their impact on marine organisms [22], satellites can measure sea surface temperature and salinity (SST and SSS) and surface chlorophyll-a, from which carbonate system parameters can be estimated using empirical relationships derived from *in situ* data. Although surface measurements may not be representative of important biological processes, e.g. fish or shellfish, observations at the surface are particularly important for OA because the change in carbonate chemistry due to atmospheric CO_2 occurs in the surface first. Thus satellites have great potential as a tool for assessing changes in carbonate chemistry.

SST has been measured from space with infrared radiometry since the 1960s, but the data are only globally of sufficient quality for climate studies since 1991 [40]. Satellite measurements of chlorophyll-*a* in the visible are more recent, starting in 1986 and delivering high quality global data since 1997 [41]. Both measurements are made globally at high spatial and temporal resolution, but with data gaps due to effects such as cloud, which can greatly affect data availability in cloudy regions. SST is measured in the top few microns, and chlorophyll-a is generally measured to depths around 1-100m, depending on water clarity. Data quality can be affected by many issues, e.g. adjacent land or ice may affect both SST and chlorophyll-a retrievals, and suspended sediment may affect chlorophyll-a retrievals.

Only since 2009 has a satellite-based capability for measuring SSS existed. Increasing salinity decreases the emissivity of seawater and so changes the microwave radiation emitted at the water surface. ESA Soil Moisture and Ocean Salinity (SMOS) and NASA-CONAE Aquarius (launched in 2009 and 2011 respectively, both currently in operation), are L-band microwave sensors designed to detect variations in microwave radiation and thus estimate ocean salinity in the top centimeter. The instruments are novel and the measurement is very challenging, and research is ongoing to improve data quality[42]. The instruments can measure every few days at a spatial resolution of 35-100km, but single measurements are very noisy, so the instantaneous swath data are generally spatially and temporally averaged over 10 days or a month, with an intended accuracy around 0.1 - 0.2 g/kg for monthly 200 km data. A particular issue close to urban areas is radio frequency interference from illegal broadcasts, which are gradually being eliminated but still result in large data gaps, particularly for SMOS.

The signal can be affected by nearby land or sea ice, and the sensitivity to SSS decreases for cold water, by about 50% from 20ºC to 0ºC [43].

With these challenges, a central question is whether satellite SSS can bring new complementary information to *in situ* SSS measurements such as Argo for assessing OA. Direct comparisons[44, 45] indicate differences of 0.15-0.5 g/kg in a 1°x1° region over 10-30 days. The two are difficult to compare directly however, as Argo measures 5m or more from the surface, so some differences are expected even in the absence of errors, especially where the water column is stratified. A better strategy might be to compare their effectiveness in estimating OA. How the uncertainties propagate through the carbonate system calculations is the subject of ongoing research.

Despite biases and uncertainties, satellite measurements of SSS in the top centimeter contain geophysical information not detected by Argo [46, 47]. In addition, Argo coverage can be much poorer than satellite SSS in several regions such as the major western boundary or equatorial currents and across strong oceanic fronts. The use of interpolated Argo products presents an additional source of uncertainty due to the interpolation scheme.[48] Satellite SSS can also resolve mesoscale spatial structures not resolved by Argo measurements[49], and unlike Argo, satellites provide a synoptic 'snapshot' of a region at a given time.

Regular mapping of the SSS field with unprecedented temporal and spatial resolution at global scale is now possible from satellites. The impact of using satellite SSS for carbonate system algorithms can now be tested, where previously there was a reliance on climatology, *in situ* or model data. For example, this provides the means to study the impact that freshwater influences (sea ice melt, riverine inputs and rain) can have on the marine carbonate system. The use of satellite SSS data will also allow evaluation of the impact on the carbonate system of the inter- and intra-annual variations in SSS.

Recent advances in radar altimetry (e.g. Cryosat-2 and Sentinel 1 satellites and sensors) are already enabling significant improvements in satellite sea-ice thickness measurements[50]. Thin sea ice thickness can now also be determined from SMOS, complementing altimeter estimates mostly valid for thick sea ice[51]. Sea ice thickness is important for OA research as it indicates whether ice is seasonal or multi-year, supporting the interpretation of carbonate parameters. Altimetry is also used to measure wind speeds and increases the coverage of scatterometer estimates in polar regions. It provides higher-resolution (along track) estimates of surface wind stress, which can potentially be used to indicate regions of upwelling. Wind-driven upwelling causes dense cooler water (with higher concentrations of CO_2 and thus more acidic) to be drawn up from depth to the ocean surface. This upwelling can have significant impacts on local OA and ecosystems [4, 52], especially at eastern oceanic boundaries [53, 54].

It is important to emphasise that the use of Earth observation data to derive carbonate parameters should not be seen as a replacement for *in situ* measurement campaigns, especially due to the current reliance on empirical and regional algorithms. Earth observation algorithms need calibration and validation with *in situ* data such as those taken by GOA-ON, and if the carbonate system response changes over time, empirical and regional algorithms tuned to previous conditions may become less reliable.

4.2 Algorithms for estimating carbonate parameters

The four key OA parameters (pCO_2, DIC, TA, pH) are largely driven by temperature, salinity and biological activity, allowing empirical relationships to be developed using *in situ* measurements of OA parameters. Table 2 shows a range of published algorithms based on such relationships, while Figure 1 shows their geographical coverage. Both illustrate that most of the literature has focused on the northern basins of the Pacific and Atlantic and the Arctic, especially the Barents Sea, with all other regions only attracting algorithms for a single parameter or none at all..[55]

Parameter	Dependencies	Region and references
pCO_2	SST	Global[56], Barents Sea[57]
	SST, SSS	Barents Sea[58], Caribbean[14]
	SST, Chl	N Pacific[59]
	SSS, Chl	North Sea[60]
	SST, SSS, Chl	N Pacific[61]
	SST, Chl, MLD	Barents Sea[62]
TA	SSS	Barents Sea[57]
	SST, SSS	Global[18, 63], Arctic[15]
	SSS, nitrate	Global[55]
DIC	SST, SSS	Equatorial pacific[64]
	SST, SSS, Chl	Arctic[15]
pH	SST, Chl	N Pacific[10]

Table 2. Example regional algorithms for each carbonate parameter illustrating the variable dependencies. Chl is chlorophyll-*a* and MLD is mixed layer depth.

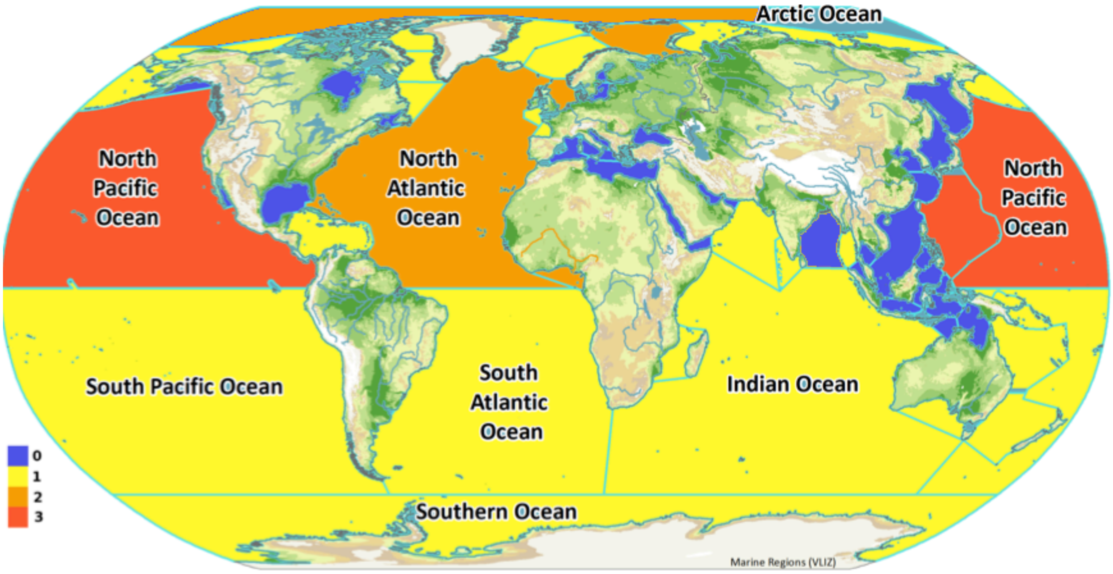

Figure 1. The number of key carbonate parameters (f_{CO2} or p_{CO2}, TA, DIC, pH) for which regional algorithms exist in the literature that can be implemented using just satellite Earth observation data. Regions are indicative of open ocean areas, as implementation of algorithms in coastal areas may be problematic.

NOAA's experimental Ocean Acidification Product Suite (OAPS) is a regional example of using empirical algorithms with a combination of climatological SSS and satellite SST to provide synoptic estimates of sea surface carbonate chemistry in the Greater Caribbean Region [14]. p_{CO2} and TA were derived from climatological SSS and satellite SST, then used to calculate monthly estimates of the remaining carbonate parameters, including aragonite saturation state and carbonate ion concentration. In general the derived data were in good agreement with *in situ* measured data (e.g. mean derived TA = 2375 ± 36 μmol kg^{-1} compared to a mean ship-measured TA = 2366 ± 77 μmol kg^{-1}). OAPS works well in areas where chlorophyll-*a* is low, however in regions of high chlorophyll-*a*, where net productivity is likely to perturb the carbonate system, and in areas where there are river inputs, the approach tends to underestimate aragonite saturation state, for example [21].

A quite different approach is the assimilation of satellite data into ocean circulation models [65]. The model output carbonate parameters can then be used directly. This allows satellite-observed effects to be extended below the water surface, albeit with the uncertainties inherent in model data. Here we seek to assess the direct use of satellite data through empirical algorithms to improve OA estimates.

4.3 Regions of interest for Earth observation

Arctic Seas

It is increasingly recognised that the Polar Oceans (Arctic and Antarctic) are particularly sensitive to OA [66]. Lower alkalinity (and thus buffer capacity), enhanced warming, reduced sea-ice cover resulting in changes in the freshwater budget [67], and nutrient limitation make it more vulnerable to future OA [68]. Retreating ice also provides increased open water for air-sea gas exchange and primary production [69].

The remote nature of the Arctic Ocean provides difficulties for collecting *in situ* datasets, with limited ship, autonomous vehicle and buoy access, and *in situ* data collection during winter months is often impossible. Therefore the use of remote sensing techniques is very attractive, if sufficient *in situ* data can be found to calibrate satellite algorithms, and if the challenges of Arctic remote sensing can be overcome. These waters are very challenging regions for satellite remote sensing. For instance, low water temperatures reduce the sensitivity range of SSS sensors [43], and sea ice can complicate retrievals of SSS and chlorophyll-*a* [70, 71]. Improvement in the accuracy of high latitude satellite SSS is expected soon by combining observations from SMOS, Aquarius and the upcoming SMAP sensor, all polar-orbiting L-band radiometers.

The Bay of Bengal

This region is clearly a focus of current OA research with unique characteristics due to the large freshwater influence. The flow of fresh water from the Ganges Delta into Bay of Bengal (42,000 m^3/sec) represents the second greatest discharge source in the world. Additionally, rainfall along with freshwater inputs exceeds evaporation, resulting in net water gain annually in the Bay of Bengal. Collectively these provide an annual positive water balance that reduces surface salinity by 3-7 g/kg compared to the adjacent Arabian Sea [72, 73], resulting in distinctly different biogeochemical regimes [74]. Biogeochemically, the Indian Ocean is one of the least studied and most poorly understood ocean basins in the world [74]. This is particularly true for the Bay of Bengal where a relatively small number of hydrographic sections and underway surface observations have been undertaken, despite the notable influence of freshwater on particle dynamics, air-sea carbon flux and surface carbonate chemistry [75-79]. North of 15° S, TA increases relative to salinity [80], indicating the presence of an important land source that can broadly affect acidification dynamics.

To date there is little work on acidification dynamics and air sea exchange of CO_2 in the Bay of Bengal [81-83]. In 2013, the Bay of Bengal Ocean Acidification (BOBOA) Mooring was deployed for the first time in Bay of Bengal (15°N, 90°E) by PMEL (NOAA) and the Bay of Bengal Large Marine Ecosystem Program (BOBLME). Data from the buoy will improve our understanding of biogeochemical variations in the open ocean environment of the Bay of Bengal.

It is an open question whether SSS can be used to estimate TA in the Bay of Bengal. An important step towards answering this question would be to investigate the spatial variability of the TA to salinity relationship in the region. Use of satellite SSS in the region is also challenged by heavy radio frequency interference.

The Greater Caribbean and the Amazon plume

The reefs in the Greater Caribbean Region are economically important to the US and Caribbean nations with an estimated annual net value of US$3.1-4.6 billion in 2000 [84]. At least two thirds of these reefs are threatened from human impacts including OA. The skeleton of a coral is made of aragonite and the growth of their skeletons is reduced by OA [6], and numerous studies have shown a net decline in coral calcification (growth) rates in accordance with declining $CaCO_3$ saturation state [85]. The waters of the Greater Caribbean region are predominantly oligotrophic and similar to the subtropical gyre from which it receives most of its water [14]. Whilst the often shallow water environments of coral reefs and the plethora of small islands can make it challenging for Earth observation instruments to collect reliable data, the oligotrophic nature and the similarities in water type across the whole region make it ideal for the development of novel products. This region therefore provides an ideal case study to develop and evaluate algorithms representative of a shallow, oligotrophic environment.

The Amazon plume, south of the Greater Caribbean, is the largest freshwater discharge source in the world (209,000 m^3/sec). It can cause SSS decreases of several units many hundreds of kilometers from land, and has an area that seasonally can reach 10^6 km^2. These characteristics make it an ideal case study for testing and evaluating remote sensing algorithms, particularly to study the space-time resolution tradeoffs using SSS sensors.

5. Future opportunities and focus

The Copernicus program is a European flagship initiative, worth more than €7 billion, which aims to provide an operational satellite monitoring capability and related services for the environment and security [86]. The launch of the Sentinel-1A satellite in 2014 signaled its start. Of the five Sentinel satellite types, Sentinels 2 and 3 are most appropriate for assessment of the marine carbonate system [87-89]. These satellites will provide chlorophyll-*a* and SST with unprecedented spatial and temporal coverage. The development of higher spatial resolution geostationary sensors that continually monitor chlorophyll-*a* and SST over the same area of the Earth also holds much potential for the future of OA assessment and research [90]. These satellites and sensors are able to provide 10 or more observations per day, allowing the study of the effect of tidal and diurnal cycles on OA. The societal importance of measuring and observing the global carbon cycle was further highlighted with the launch of the NASA Orbiting Carbon Observatory (OCO-2) in 2014. This satellite and its sensors are designed to observe atmospheric CO_2 concentrations, but its potential for marine carbon cycle and OA is likely to be a focus of future research.

SMOS and Aquarius have recently passed their nominal lifetimes, with SMOS now extended until 2017. Based on the lifetimes of previous satellite Earth observation sensors, they may well operate until the early 2020s. NASA's SMAP satellite, to be launched in January 2015, should provide short-term continuity. The development of the technology and the clear importance of monitoring ocean salinity are likely to support the development of future satellite sensors. Also, historical time series data from alternative microwave sensors hold the potential for a 10+ year time series of satellite based SSS observations [91], and this sort of measurement record is likely to extend into the future as it forms the basis of a global SSS monitoring effort.

In summary, satellite products developed up to now in the OA context have been regional, empirical or derived with a limited variety of satellite datasets, rendering an effort to systematically exploit remote sensing assets (capitalizing on the recent advent of satellite salinity measurements) absolutely timely. To-date there is only regional application of satellite SST to address the issue of assessing OA [62], along with two non-peer-reviewed attempts to calculate carbonate system products using satellite SSS data [92, 93]. Supported by good *in situ* measurement campaigns, especially in places with currently poor *in situ* coverage such as the Arctic, satellite measurements are likely to become a key element in understanding and assessing OA.

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