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## Background

The Earth system has entered a new geological epoch, the *Anthropocene*. The oceans' capacity to regulate atmospheric carbon dioxide ( $\text{CO}_2$ ) at various timescales is amongst the most crucial players to maintain climate on Earth in a habitable range. The biogeochemical property exerting this regulatory mechanism is *alkalinity*, the oceans'  $\text{CO}_2$  and pH buffer capacity. The proposed project will investigate how the oceans' alkalinity is impacted firstly by human measures, required by the Paris agreement (COP 21) to mitigate climate change via bioenergy production and its downstream effects on shallow oceans, and secondly by climate change, in particular by increased weathering in the Arctic because of ice retreat.

## Objectives

**Objective 1:** We will investigate how future bioenergy production, as required in all of the SSPs supporting the Paris agreement, will affect the coastal oceans, in particular  $\text{CO}_2$  and pH conditions, in order to allow for a sustainable implementation of this measure, without detrimental or possibly disastrous effects of the shallow marine environment and their ecosystems. In detail **we will investigate how variable nitrogen-nutrient inputs to the North Sea affect metabolic alkalinity production in surface sediments and in the Wadden Sea**, and subsequently pH control and  $\text{CO}_2$  buffering. We will employ a multi-faceted strategy comprising field observations, laboratory experiments and modeling to achieve this objective.

**Objective 2:** We will investigate the magnitudes of fluxes of weathering alkalinity into the Arctic Ocean, and assess the impacts of these processes on  $\text{CO}_2$  and pH buffering. We will address the question of how sensitive these processes are to climate and anthropogenic forcing. We will employ terrestrial cosmogenic nuclides and marine carbonate system data to address this objective.

{In technical terms: Investigations of anthropogenically driven non-linearities in the alkalinity-salinity relationship of the oceans.}

## Progress

- Various research cruises in 2019 (3x *RV Ludwig Prandtl*, 1x *RV Heincke*)
  - Alkalinity samples (water column, bottom & pore water)
  - Denitrification batch core incubations (sediment - water column interface)
  - Nutrient samples
  - Radium activities in surface and pore water
  - Metals, sulfur, nutrients in pore water

## Methods

- Alkalinity via Vindta
- $\text{N}_2$  production via MIMS
- Isotopic composition of  $\text{NO}_3^-$  ( $\delta^{15}\text{N}-\text{NO}_3^-$  &  $\delta^{18}\text{O}-\text{NO}_3^-$ ) via MS
- Nutrients via Autoanalyzer
- Metals via ICP-MS
- Sulfur measurements via photometer
- Short-lived radium isotopes via RaDeCC



Fig. 1: *RV Heincke* docked in the harbour of Bremerhaven in September 2019.

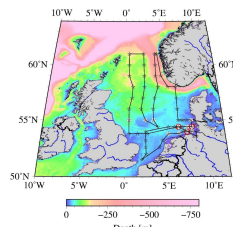


Fig. 2: The North Sea including the German Bight, the Wadden Sea and their depth profiles. Already sampled stations are marked with dots, planned stations are marked with stars.

## Outlook

- TSS-Spiekeroog
  - Alkalinity,  $\text{pCO}_2$ , pH sensor
  - $\text{CO}_2$  fluxes via eddy covariance
- Arctic
  - Selection of study sites and field expedition
- North Sea & Ems & Elbe
  - Various research cruises
- Coupled hydrodynamic ecosystem model
- Additional alkalinity producers (Fe, Mn, S)

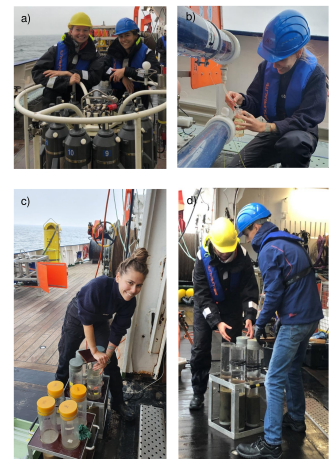


Fig. 3: Photos from cruise HE541 during the sampling: a) with the CTD rosette, b) alkalinity sampling with bottom water scoop, c) cut out mini cores for batch core incubations, d) pore water cores.

## Alkalinity - Denitrification coupling:

Denitrification, an anaerobic microbial process in which organic matter is respired using  $\text{NO}_3^-$  instead of  $\text{O}_2$  as a terminal electron acceptor. During denitrification  $\text{NO}_3^-$  is sequentially reduced to  $\text{N}_2$  and metabolic alkalinity is released as "by-product". Denitrification increases due to eutrophication which results from the usage of fertilizers in agriculture. Leaching of unused nutrients via ground water into rivers leads to higher nitrate inflows into the Wadden Sea, German Bight and North Sea. An increase in denitrification therefore leads to an enhanced buffer capacity and consequently to an enhanced alkalinity. The detection of denitrification in the interface between bottom water and sediment is based on the Isotope Pairing Technique (IPT) combined with batch core incubations.  $\text{N}_2$  production will be analyzed following the addition of labelled nitrate. All three isotope species of  $\text{N}_2$  ( $^{28}\text{N}_2$ ,  $^{29}\text{N}_2$  and  $^{30}\text{N}_2$ ) will be analyzed to quantify  $\text{N}_2$  production by denitrification. An concurrent potential increase in alkalinity will be assessed as well.

## Enhanced erosion in the Arctic:

The Arctic is most susceptible to climate change. To test whether the transport of weathering products of alkalinity-bearing rocks to the Arctic Ocean is increasing due to climate change, a pre-industrial erosion rate will be compared to the current one by using the terrestrial cosmogenic nuclide (TCN)  $^{36}\text{Cl}$  and the fallout nuclides  $^{239+240}\text{Pu}$ , respectively. TCNs are produced in-situ in minerals close to the Earth's surface via nucleonic spallation and muogenic reactions, cosmic rays being the initiators for these reactions. If an investigated system is at steady-state, the production of TCNs is equal to its loss due to denudation and radioactive decay. Thus, higher TCN concentrations indicate lower erosion rates, allowing for longer accumulation times of TCNs in the bedrock, and lower concentrations correspond to higher erosion rates. Pu isotopes are used to determine current erosion rates, averaged over the last ~50 years, since they were deposited on the Earth's surface during the nuclear weapons tests between 1952 and 1964.

## TSS-Spiekeroog:

The Time Series Station Spiekeroog will be used to detect high frequency (hourly to annual) tidally influenced changes in different carbon related values, i.e. alkalinity,  $\text{pCO}_2$  and pH. Furthermore, the impact of metabolic processes on the exchange of  $\text{CO}_2$  fluxes between the surface and the atmosphere will be investigated via eddy covariance. At TSS a nitrate and other autonomous sensors have been operational for a number of years.

Partners of the consortium (so far):