

Short Term Scientific Mission (STSM)

Scientific Report

Benthic Fluxes of ALlkaLinity in the Gulf of Cádiz (BEFALL)

By Roberta Guerra

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Grantee name:	Roberta Guerra
Institution:	University of Bologna, Inter-Departmental Centre for Research in Environmental Sciences (CIRSA)
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Purpose of the STSM

Despite covering only ca. 7% of the oceanic surface area, coastal seas contribute to about 10% to 20% of the global oceanic CO₂ uptake. Recent studies have discussed the potential importance of alkalinity production in shallow coastal sediments to the global ocean alkalinity budget, suggesting that the benthic alkalinity source could act as negative feedback to rising atmospheric CO₂ conditions and ocean acidification (Thomas et al. 2009; Brenner et al. 2015). This benthic source of alkalinity to the overlying water column has mainly been attributed to anaerobic degradation pathways of deposited organic matter.

The Gulf of Cádiz (GoC) is a domain of significant interest, and plays an important role in the carbon cycle of the North Atlantic Ocean and the Mediterranean Sea (Rodríguez-Gálvez et al. 2009; Ribas-Ribas et al. 2011). The coastal areas within the GoC are heterogeneous, thus the significance of coastal sediments to the ocean alkalinity budget in the GoC is strongly dependent on a biogeochemical transformations and fluxes in shallow sediments. Previous research suggests that coastal areas within the Gulf of Cádiz act as a source of CO₂ to the atmosphere (de la Paz et al. 2008; Burgos et al. 2018). Conversely, the limited data on benthic alkalinity fluxes from the shallow coastal areas in the GoC contrasts with the potential significance of coastal marine sediments for the carbon cycle of the GoC and the North East Atlantic Ocean.

The overall aim of the Short Term Scientific Mission (STSM) BEFALL was to increase the understanding on the biogeochemical fluxes of alkalinity in selected shallow coastal areas within the GoC. To this end carbonate and non-carbonate constituents of TA have been quantified in near-bottom and sediment pore waters, and biogeochemical fluxes of sedimentary alkalinity and nutrients have been estimated in selected coastal areas within the GoC.

Description of the work carried out during the STSM

The STSM BEFALL work was focused on bottom waters and sediment cores previously collected in target coastal areas in the Bay of Cádiz within the GoC, the Rio San Pedro and Sancti Petri Channel (36.4101° N, 6.1103° W). During the first phase of the STSM BEFALL, concentrations of carbonate and non-carbonate (ammonia, phosphate, silicate, and sulfate) components of total alkalinity (AT) have been determined at the Faculty of Marine and Environmental Sciences (University of Cadiz, Spain).

Instrumental analysis of the carbonate and non-carbonate constituents of AT in bottom waters and sediment pore waters have been conducted according the following methodologies:

1. Nutrient analysis (ammonium, phosphate and silicate) by classic spectrophotometric methods (Grasshoff et al. 1999) using a segmented flow analyzer (Skalar, San Plus);
2. Chloride, sulfate, and calcium (Cl⁻, SO₄²⁻, Ca²⁺) by High Performance Ion Chromatography (Methrom 881/ 882, Compact IC pro);
3. pH was measured in 2 mL of pore water and 100 mL of bottom water using a glass-combined electrode (Methrom) calibrated in the total pH scale using a TRIS buffer solution (DelValls and Dickson 1998). TA was computed from the titration curve with 0.1 M HCl by means of the equivalent volume (Methrom, 905). DIC and partial pressure of CO₂ (pCO₂) were computed from TA and pH, using the K1 and K2 acidity constants

proposed by (Lueker et al. 2000) in the total pH scale using the CO2SYS program (Lewis and Wallace 1998). All samples have been analyzed in duplicate, and AT measurements were validated with reference standards obtained from A. Dickson (Scripps Institute of Oceanography, San Diego, USA) to an accuracy of ± 3 mmol/kg.

Sediment pore water was obtained from 1-cm thick sediment core layers by centrifugation in a nitrogen atmosphere (30 min, 9000 g, and 10° C). Sediment porosity (Φ) was determined from water content [%] and bulk density after drying at constant weight at 105°C.

The second phase of the STSM BEFALL have been focused on the estimation of the benthic fluxes of alkalinity at the sediment/water interface in the selected coastal areas within the GoC.

The fluxes of AT (J_{Alk}) were calculated as the sum of fluxes of individual components of total alkalinity (1) according to the Fick's first law (2):

$$J_{Alk} = J_{CO_3^{2-}} + J_{HCO_3^-} + J_{HPO_4^{2-}} + J_{NH_3} + J_{SiO(OH)_3^-} + J_{HSO_4^-} + J_{B(OH)_4^-} \quad (1)$$

$$= -\Phi D_s \delta C / \delta z \quad (2)$$

where J is flux [$\mu\text{mol}/\text{m}^2 \text{ d}$], Φ is the sediment porosity and D_s is the molecular diffusion coefficient in sediment [$10^{-6} \text{ cm}^2 \text{ s}^{-1}$] (Li and Gregory 1974).

Data obtained using mass-conservation equations and the equilibrium relationships between various species, as well as estimated fluxes were subject to critical review with Prof. Teodora Ortega Diaz resulting in 5 half-day meetings during the STSM BEFALL.

Description of the main results obtained

In general, the concentrations biochemical parameters (ammonium, phosphate and silicate) measured in sediment pore water were higher than in near-bottom water, and increase with increasing sediment depth in the studied coastal areas within the GoC. Sulfate and calcium display an opposite trend with concentrations decreasing with sediment depth. Ammonium, phosphates and silicates concentration in pore water are higher at the Rio San Pedro (mean: 375 $\mu\text{mol kg}^{-1}$, 31 $\mu\text{mol kg}^{-1}$, and 106 $\mu\text{mol kg}^{-1}$, respectively) than at the Sancti Petri Channel (mean: 340 $\mu\text{mol kg}^{-1}$, 4.0 $\mu\text{mol kg}^{-1}$, and 58 $\mu\text{mol kg}^{-1}$, respectively).

In general, AT concentration measured in pore water increased with sediment depth and is higher at Rio San Pedro than at the Sancti Petri Channel (3090 - 21,240 $\mu\text{mol kg}^{-1}$ and 2900 - 6130 $\mu\text{mol kg}^{-1}$, respectively). Total concentration of non-carbonate alkalinity (N-CIBs) in pore water followed the same trend, varying between 8.2 - 186 and 8.3 - 52 $\mu\text{mol kg}^{-1}$, respectively. N-CIBs accounted for 0.3 - 1.3 % of AT at Rio Sand Pedro, and 0.3 - 0.9% of TA at the Sancti Petri Channel.

Our results show that sediments in the coastal areas in the Bay of Cadiz within the GoC can be a source of alkalinity (J_{Alk}) to the GoC (280 - 2900 $\mu\text{mol m}^{-2} \text{ day}^{-1}$) in agreement with AT fluxes found in other coastal ecosystems of the Iberian Peninsula and the Baltic Sea, but lower than alkalinity effluxes measured in the North Adriatic and the North Sea (Table 1).

The estimated coastal AT efflux was dominated by carbonate alkalinity ($J_{HCO_3^-} + 2J_{CO_3^{2-}}$) (*270 - 2870 $\mu\text{mol m}^{-2} \text{ day}^{-1}$). $J_{HCO_3^-} + 2J_{CO_3^{2-}}$ efflux was similar to the diffusive fluxes estimated in other coastal areas of the Iberian Peninsula. The contribution of non-carbonate inorganic bases (N-CIBs) to

the JAlk flux was low and accounted for 1 – 3% at the Rio San Pedro and at the Sancti Petri channel, respectively (c.a. 8 – 30 $\mu\text{mol m}^{-2} \text{day}^{-1}$).

Table 1. Benthic fluxes (J) of total alkalinity (AT) and DIC in the coastal areas of the GoC and other coastal seas. J is expressed as $\mu\text{mol}/\text{m}^2 \text{d}$.

Area	JAlk	DIC	Reference
Bay of Cadiz	280 - 2900	*270 - 2870	This work
Iberian peninsula	-	1200 - 11600	(Forja et al. 2004)
Cantabrian Sea	0 - 2400	600 - 2700	(Ortega et al. 2005)
Tinto–Odiel system	1500 - 7300	7500 - 9000	(Ortega et al. 2008)
North Adriatic Sea	-	12200 - 25200	(Hammond 1999)
Baltic Sea	727 - 2270	-	(Gustafsson et al. 2019)
North Sea	0 - 21400	0 - 29100	(Brenner et al. 2015)

On a global scale, Krumins et al. (2013) estimated an AT flux for the coastal ocean of 29 Tmol yr^{-1} . Considering our two coastal ecosystems have a surface area of about 1 and 10 km^2 , estimated total AT input to the coastal ocean in the GoC is ca. $2 \cdot 10^6 \text{ mol yr}^{-1}$. Overall, the STSM BEFALL results show that sedimentary alkalinity generation should be regarded as a key component in the CO_2 dynamics of the coastal ocean within the GoC.

To better constrain the main pathways of alkalinity generation in the sediment, and to quantify how sedimentary alkalinity drives atmospheric CO_2 uptake in the heterogeneous coastal ocean within of GoC, further in-situ measured data is needed at extended regional scale.

Future collaborations

The STSM recipient organized one meeting with the local coordinator of the EU ERASMUS Mundus Master WACOMA (WATER and COastal MAnagement) Prof. Irene Laiz in the view of expanding the research topics for the master students including climate change and impacts on the Arctic and Antarctic Oceans.

Further research and dissemination of the outcomes obtained with the STSM BEFALL will include:

- Strengthening the cooperation between the School of Sciences at the University of Bologna and the Faculty of Marine and Environmental Sciences at University of Cadiz (Spain) through exchanges of teaching staff, PhD and Master students with a focus on research topics linked with *ocean, climate change and acidification* under the ongoing Erasmus plus agreement between the two Universities.
- Strengthening the cooperation between the CIRSA - University of Bologna, the Faculty of Marine and Environmental Sciences - University of Cadiz (Spain) through exchanges of teaching staff and overseas students from the Erasmus Mundus Master WACOMA (Water and Coastal Management) on research topics lined with *ocean, climate change and acidification*; the physical oceanographer Prof. Irene Laiz (UCA) will be the reference person at the UCA.

- Presentations of the results obtained with the BEFALL STSM at the next WHOI Ocean Biogeochemistry Summer Workshop (24 – 27 June, 2019, Woods Hole, MS); co-author an original research article to be submitted to a peer-reviewed journal by early 2020.

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